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HAZARDOUS WASTE COMBUSTION IN INDUSTRIAL PROCESSES: CEMENT AND LIME KILNS

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The parameters examined in this report were Destruction and Removal Efficiency (DRE) of the Principal Organic Hazardous Constituents, particulate and HCl emissions, metals, and the effect of burning hazardous waste on SO_2, NO_x, and CO emissions. The primary conclusion of this study is that DRE's of 99.99% or greater can be obtained in properly-operating calcining kilns. Particulate matter can increase when chlorinated wastes are burned in a kiln equipped with an electrostatic precipitator. Those kilns equipped with fabric filters showed no change in emissions.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the need of both large and small businesses in handling their wastes responsibly and economically.

This report will be useful to EPA's Office of Solid Waste and Emergency Response, U.S. EPA Regional Offices, and State and Local Environmental Permit Writers. It contains a review and summary of all environmental assessments of hazardous waste combustion in calcining kilns.

Thomas R. Hauser, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

This report summarizes the results of several studies relating to hazardous waste combustion in cement and lime kilns. The tests included in this study are four kilns tested by the U.S. Environmental Protection Agency, four kilns tested by State agencies or the kiln operator, two Canadian tests, and one Swedish test. The predominant types of wastes tested included chlorinated organic compounds, aromatic compounds, and metal-contaminated waste oil. The kiln types include lime kilns and cement kilns, which included the dry, wet, and preheated processes. Fabric filters and electrostatic precipitators (ESPs) were the pollution control devices used in these processes, and the primary fuels included coal, coke, coal/coke, fuel oil, and natural gas/coke.

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1.0 INTRODUCTION

Preliminary feasibility studies and tests have indicated that some industrial facilities with high-temperature combustion processes may provide a cost-effective and environmentally acceptable alternative to the disposal of hazardous wastes in incinerators or landfills. These industrial processes have the potential for recovering the heating value of the waste, removing chlorides, and providing a destruction and removal efficiency (DRE) equivalent to hazardous waste incinerators.

Several industrial processes can provide temperatures and residence times similar to those required for hazardous waste incinerators. Examples include cement, lime, and aggregate kilns, industrial boilers, and blast furnaces. Cement and lime (calcining) kilns are of particular interest because of their potential for reducing the environmental impact of disposal in a cost-effective manner. The promising characteristics of calcining kilns include:

- Existing high-temperature combustion process at 1,350° to 1,650° C (2,500° to 3,000° F) with a gas residence time on the order of seconds.
- Large number of plants scattered throughout the country, which could potentially handle large quantities of combustible hazardous waste liquids.
- Large-scale equipment in place, including process control and pollution control; relatively small capital investment required.
- Instantaneous temperature excursions unlikely because of the huge thermal inertia.
- The alkaline environment in the kiln absorbs HCl from chlorinated waste combustion.
- Kilns are operated under draft (slight vacuum); therefore, there would be little outward leakage of fumes, mostly inward leakage of air.

- Noncombustible hazardous components may be retained in the process solids.

- Energy savings from substitution of waste fuel for oil, coal, or gas.

The combustion of hazardous waste in kilns has been investigated in Canada,[1] [2] Sweden,[3] [4] and Norway[5] as well as in the U.S. Papers have been published that promote calcining kilns as a method of waste disposal that is better than current practices, particularly for chlorinated organics.[6] [7] Papers have also been published that warn of actual and potential risks associated with waste combustion.[8] Several kilns have been tested during waste combustion to provide more data on the effects of waste combustion. Some of these tests have been comprehensive in their attempt to determine effects on emissions, product quality, fate of metals and chlorine, and products of incomplete combustion. The test results are used in this report to:

- Present DREs of principal organic hazardous constituents (POHCs).

- Compare baseline operation (no waste fuel burned) to the operation with waste fuel.

- Determine what products of incomplete combustion (PICs) are formed.

- Examine the fate and distribution of metals.

- Examine the effect of waste burning on HCl emissions, and determine the fate and distribution of chlorine.

- Examine the effects of waste fuel burning and process conditions on other pollutants (e.g., particulate matter, NO_x, SO_2, total hydrocarbons).

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

DREs of > 99.99 percent are generally achievable in properly operating calcining kilns. This level of DRE has been achieved at different types of kilns with a variety of difficult-to-destroy wastes. Baseline, background, and contaminant levels of the target POHCs imply the DREs are probably conservative, as are the estimates of POHC emission rates. The high DREs for spiked POHCs (such as Freon 113), which are unique to the waste fuel and generally less susceptible to background or blank problems, support this conclusion. The lowest measured emission rates and highest DREs were found at two kiln tests (Stora Vika and Rockwell Lime) that apparently had the least interference from background levels or contamination.

A small increase in PIC emissions was observed during the waste burns at some kilns, and at others no differences were noted between baseline and waste fuel burns. PICs can increase at a poorly operating kiln whether it is fired with waste fuel or not. PICs from the primary fuel, especially coal, have been identified and their emission rates appear to be independent of waste combustion within the accuracy of the emission measurements.

The tests for particulate matter indicate that particulate matter emissions can be controlled when chlorinated wastes are burned and do not necessarily increase. Two tests at kilns equipped with ESPs (chloride input up to 4 kgCl/Mg clinker) and two tests at kilns equiped with fabric filters (average chloride input up to 5.5 kgCl/Mg clinker) showed no increase in particulate matter emissions when chlorinated wastes were burned. Extensive tests at St. Lawrence Cement and Store Vika indicated that controlled particulate matter emissions increased as the chloride loading increased. The increase may be limited by altering the ESP to compensate for changes in the dust resistivity, controlling chloride input, and altering the chloride cycle in the kiln.

HCl emissions increase as the chloride loading increases; however, generally over 90 percent, and in several cases over 99 percent, of the additional chlorine entering the kiln is retained in the process solids (waste dust and clinker). Most of the additional chloride is removed with the waste dust, and several plants increased the rate of waste dust removal to aid in controlling the chloride cycle. Chloride accumulation, although probably variable from kiln to kiln, appears to start in the range of 6-9 kgCl/Mg clinker with a tendency toward ring formation at the upper end of the range.

Lead emissions and the lead concentration in the waste dust increase when chlorinated wastes contaminated with lead are burned. However, baseline emission rates of lead are low to begin with and total lead emissions during waste combustion are roughly comparable to the lead emissions from several automobiles burning leaded gasoline. The calcining kiln has the potential to retain over 99 percent of the lead entering the kiln in the process solids (waste dust and clinker). In comparison, a boiler burning waste oil retains less than 50 percent of the lead, and probably retains even less because of losses during soot blowing.

SO_2 emissions are generally decreased when the waste fuel replaces a sulfur-containing fuel. SO_2 emissions were found to be a function of several variables, such as sulfur loading, oxygen input, and temperatures. Cement kilns can be operated to obtain low SO_2 concentrations. Lime kilns are operated at higher SO_2 levels deliberately to avoid sulfur in the lime product.

NO_x emissions are not significantly affected by waste combustion. NO_x concentrations vary over time at the same kiln and are affected by oxygen input, primary to secondary air ratio, and temperatures. Continuous monitors for NO_x respond rapidly to process changes.

Emissions of carbon monoxide, especially during coal combustion, can exhibit short-lived spikes and are generally indicative of combustion stability. Total hydrocarbon emissions increased at several plants during waste combustion and were not significantly different at others; hydrocarbon concentrations below 10 ppm were generally observed.

2.2 RECOMMENDATIONS

All emission tests should collect an adequate number of background and blank samples because the required low detection levels are easily biased high by low level contamination. The testing personnel should be aware of and account for other sources of the POHCs, such as process water, coal combustion, and contamination.

As chlorinated waste combustion continues, more information should be gathered on the chloride and sulfate cycles in the kiln. Guidance may then be provided to other operators on controlling the cycle, minimizing HCl and SO_2 emissions, and controlling the dust loading on the pollution control device. General guidance is currently available, but quantitative guidance could be developed. The operator has additional incentive to obtain the information to prevent chloride or sulfate ring formation, corrosion of equipment, and to maintain product quality.

Continuous monitors for NO_x and SO_2 show great promise for kiln control, optimization of combustion conditions, and emission control. A study of controlled process changes in conjunction with the continuous monitors could yield information that is useful to both the operator and regulatory agency. Improved and more consistent kiln operation could result in lower emissions at calcining kilns whether wastes are burned or not.

Finally, at some point in the future a comparative analysis of technologies available for hazardous waste disposal should be conducted. The study should provide the facts, alternatives, and recommendations for the benefit of State agencies, the public, waste generators, and waste disposers.

3.0 CEMENT AND LIME PRODUCTION

3.1 OVERVIEW

Portland Cement

Portland cement is one of the largest mineral commodities produced in the United States with an annual production capacity in 1982 of 79 million Mg/yr. This capacity was owned by 46 companies with the top 10 accounting for 59 percent of the total capacity. A total of 135 plants with 274 kilns are located throughout 38 states. The kilns are quite variable in capacity and range in size from less than 45,000 Mg/hr up to 1.7 million Mg/hr. There is a trend toward larger plants because of better efficiency and lower capital requirements per ton of product. From 1950 to 1975, the average plant capacity increased from 305,000 Mg/hr to 487,000 Mg/hr.[9]

The cement industry is very capital intensive and is dependent upon the construction industry. Energy costs normally amount to 33-40 percent of the total cost of cement manufacture, but may be as high as 65 percent. Energy efficiency improvements have been made since 1950 when about 7.8 million BTUs were required per ton of product. The estimate for 1979 was 6.1 million Btus per ton, and this figure has probably continued to decline based on the historical trend. In 1972, only 39 percent of the industry's energy was supplied by coal, but conversion to coal was started in the 1970s.[9] Currently, over 90 percent of the installed capacity uses coal as the primary fuel.

Lime

Lime production in the U.S. was over 18 million Mg/hr in 1979. Lime is used in various industries, such as steelmaking (36 percent), water purification (8 percent), alkalies (6.5 percent), and pulp and paper manufacture (5.5 percent). The lime is produced by 60 companies at 155 plants located in 41 states. These plants include a total of 450 kilns. The top 10 of the 60 companies generate about one-half of the total lime production.[10]

The production of lime also requires significant energy input at an estimated rate of 7 million Btu/ton of lime. The primary sources of energy are coal and coke (70 percent) and natural gas (23 percent),[10] The lime kilns are also obvious candidates for savings in fuel cost from the burning of wastes as supplemental fuels.

3.2 PROCESS DESCRIPTION

3.2.1 Cement Kilns

Portland cement is produced by the controlled high-temperatures drying of a carefully proportioned mixture of finely ground limestone, silica, alumina, and iron oxide in a rotary kiln. The solid discharged from the kiln is called clinker and is a chemically complex mixture of calcium silicates, aluminates, and ferrites. This clinker is ground and blended with 2 to 5 percent calcium sulfate (gypsum) and is sold as Portland cement.

The basic raw materials are generally extracted from a quarry at or near the cement plant and are composed of limestone, cement stone, shale, clay, sand, and iron ore. The quarry rock is crushed in primary and secondary crushers for size reduction and is then stored in silos prior to mixing with other raw materials (such as clay, silica, alumina, or iron ore). The kiln feed is prepared by proportioning, grinding and blending these raw materials to a consistent and homogeneous composition. The composition of typical raw materials used for cement manufacture are given in Table 3-1.[1]

The three most prevalent types of cement processes are the wet, dry, and dry with preheater. The oldest of the three processes is the wet process in which the raw materials are proportioned, ground with water in a raw mill, and then slurried with 30 to 40 percent water. In the more recent dry process, the moisture content of the raw materials is reduced to less than one percent before or during grinding and the dry powder (about 200 mesh) is fed directly to the kiln. Originally, the wet process offered advantages in ease of handling, mixing, and blending the raw materials in slurry form, which aided in maintaining a high quality product. However, improvements in the handling and blending of dry bulk solids, coupled with the lower energy requirements of the dry process, have resulted in a trend away from the wet process.[9] An even more recent trend toward reducing energy requirements uses a preheater with a dry raw material feed. The

TABLE 3-1. TYPICAL COMPOSITIONS OF RAW MATERIALS USED IN CEMENT MANUFACTURE[1]

Material	Percent by weight				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Limestone	5.7	0.8	0.3	52.0	0.4
High silica limestone	36.8	1.8	0.6	33.6	0.5
Cement stone	18.0	5.0	1.5	40.0	2.0
Shale	53.8	18.9	7.7	3.2	2.2
Sand	70.0	15.0	5.0	0.8	0.2
Clay	61.0	16.9	12.4	0.5	0.4

preheater uses the hot kiln exhaust gases in a countercurrent flow system to heat and precalcine the dry feed before it enters the kiln. The approximate heat consumptions of the wet, dry, and preheater processes are 5.8, 4.6, and 3 million BTUs/ton, respectively.[1]

Figures 3-1 and 3-2 are schematics of wet and dry process cement kilns. The kiln is an inclined (3 to 6°) cylinder lined with refractory brick with typical sizes that range from 60-760 ft in length and 6-25 ft in diameter.[9] The raw material feed enters the upslope end of the kiln and travels down through the various drying and reaction zones as the kiln rotates. The first portion of the upslope end often contains chains to aid in heat transfer and mixing. The solids then pass through the calcining zone where CO_2 is dissociated from calcium carbonate. The last section of the kiln is the clinkering or sintering zone where a strongly exothermic reaction between CaO and SiO_2 forms dicalcium silicate and where an endothermic reaction between dicalcium silicate and CaO yields tricalcium silicate, which is the primary hydraulic material in cement.

The clinker is formed at 2500 to 2600° F and then leaves the kiln and enters the clinker cooler where air is passed through moving grates to cool the product. The solid's residence time varies from kiln to kiln and is controlled by the kiln's revolutions. Typical solids residence times are on the order of 2 (range of 1 to 4) hours.[9]

The kiln is fired at the downslope end and the gases travel upslope countercurrent to the solid's flow. Primary air and a portion of the preheated secondary air from the clinker cooler are used as the combustion air. The gas residence time is on the order of seconds and gas temperatures typically approach a maximum of 3,000° F. Residence time calculations by Weitzman show a gas residence time of over 3 seconds at temperatures of 2000° F or higher and over 8 seconds at temperatures over 1500° F.[11] (Estimates of residence time are likely to vary from kiln to kiln.)

Figure 3-3 shows the steady-state temperature and concentration profiles in a kiln based on a mathematical simulation of the process.[12] Note that gas temperatures (Tg) are always higher than the solids temperature (T_s). The gas temperature increases (starting from the feed end) fairly constantly; however, the solid's temperature remains steady in this wet

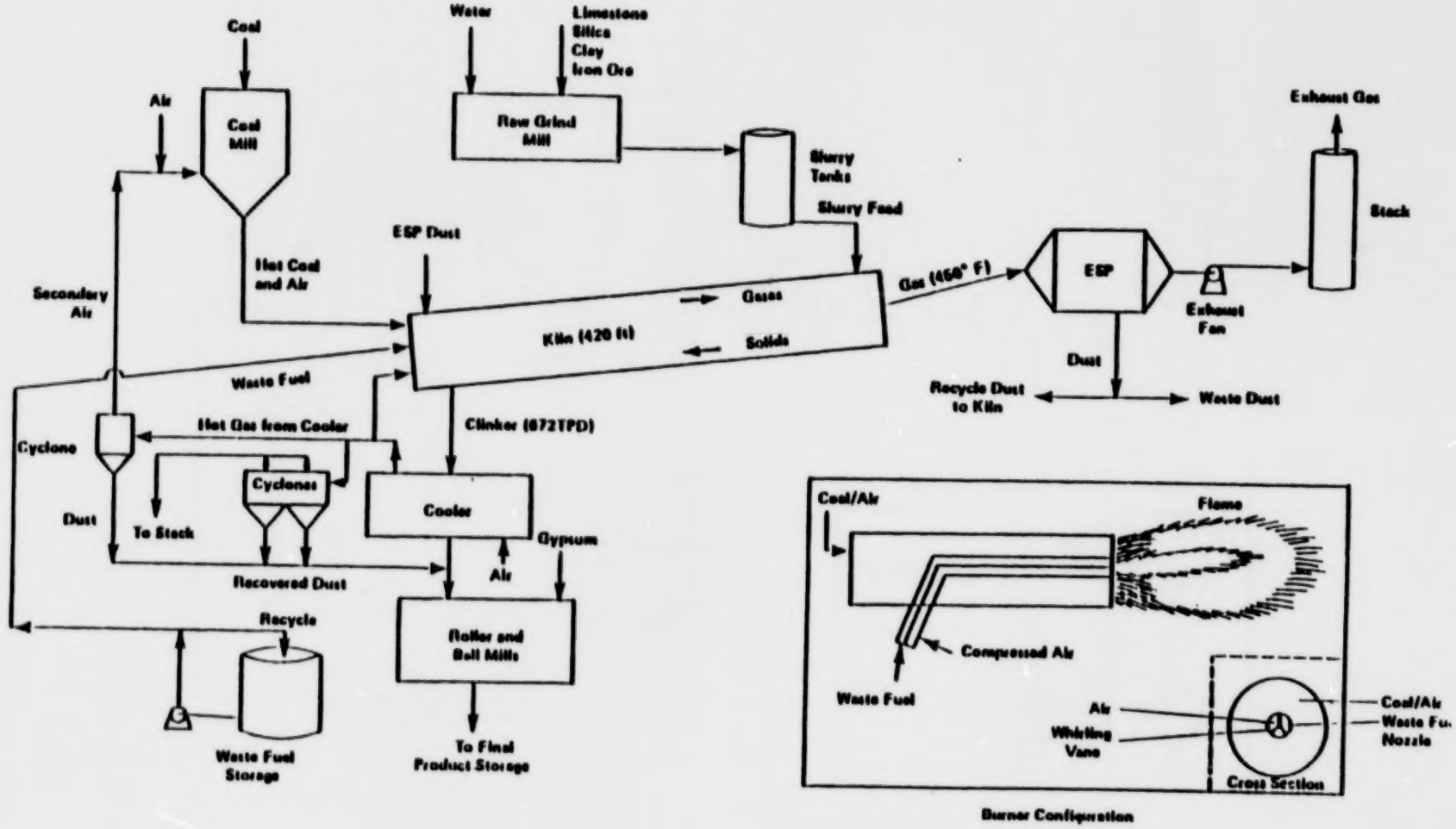

Figure 3-1. Wet process cement kiln[19].

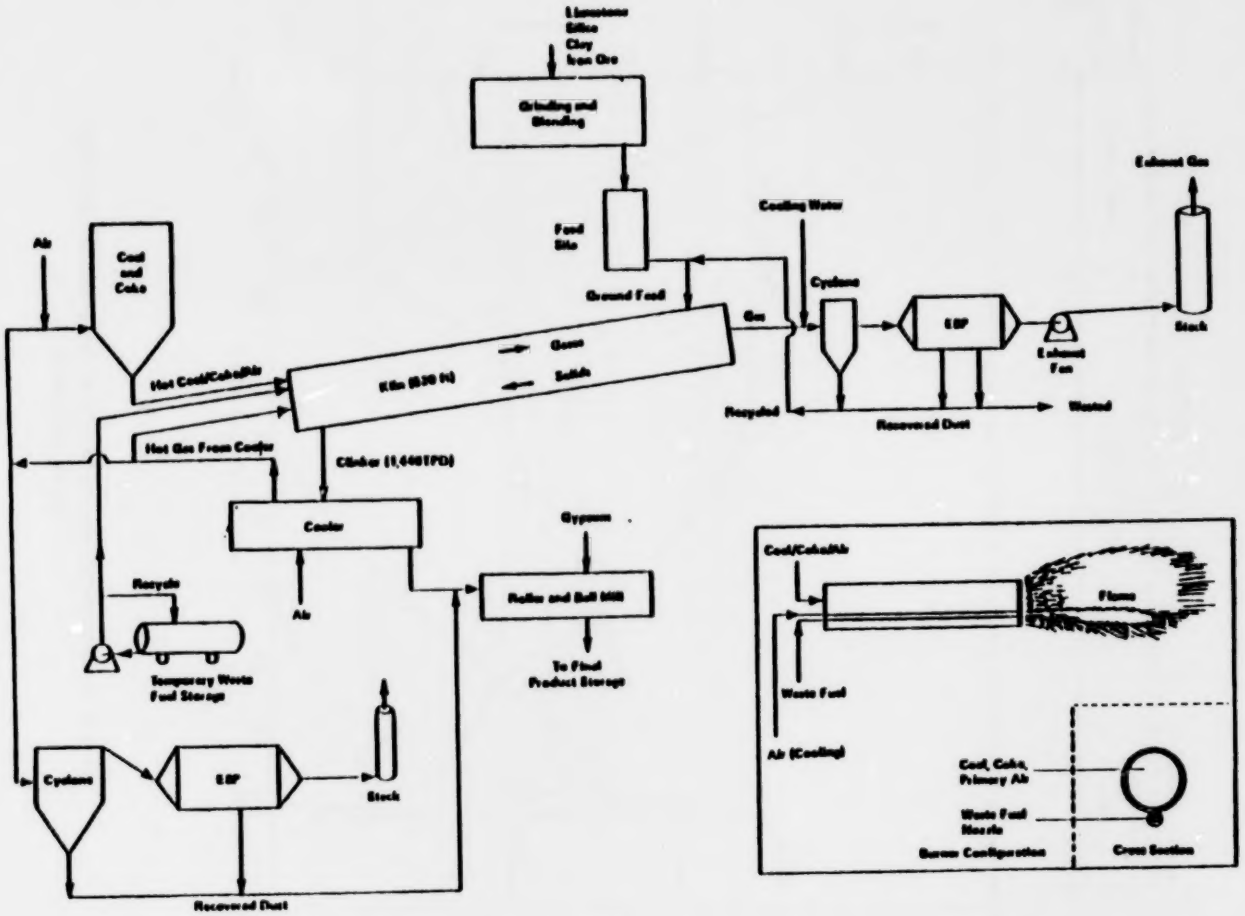

Figure 3-2. Dry process cement kiln[16].

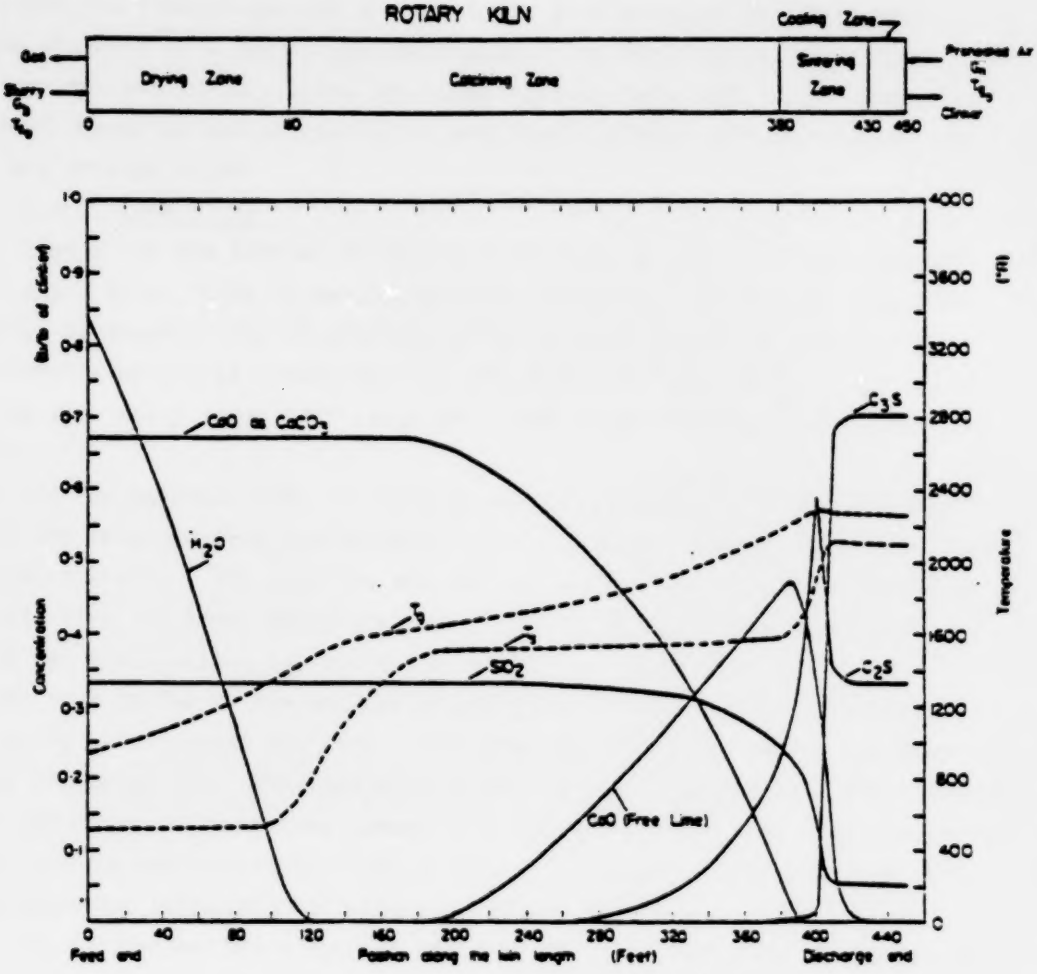

Figure 3-3. Steady-state temperature and concentration profiles along kiln length[12].

process kiln until most of the water is removed. The next significant increase in solid's temperature occurs in the clinkering or sintering zone.

The most common types of air pollution control devices that are used to clean the exhaust gas are electrostatic precipitators and baghouses, often preceded by a centrifugal separator. The distribution of control devices for wet and dry kilns are summarized in Table 3-2. ESPs appear to be most common at wet process kilns and fabric filters are more common at the dry process kilns.

3.2.2 Lime Kilns

Lime kilns are similar to cement kilns through the calcining zone of the cement kiln. Lime is manufactured by calcining high quality limestone ($CaCO_3$) at temperatures of 2400° F, which volatilizes nearly half of the limestone's weight as carbon dioxide (CO_2) to form lime (CaO). Lime kilns are mostly rotary kilns that range up to 500 ft in length and 17 ft in diameter.[10]

The raw material feed includes carbonates of calcium and magnesium, which are obtained from quarry deposits of limestone, marble, chalk, dolomite, or oyster shells. The quarries are chosen to provide low concentrations of silica, clay, or iron, which are impurities. The stone is crushed and sized and often washed to remove contaminants. The crushed and sized quarry rock is fed to the upslope end of the kiln and heated to liberate CO_2 as it travels down the kiln. The lime product is removed at the downslope discharge end. The lime kiln is operated at temperatures (2000-2400° F) that are somewhat lower than cement kiln temperatures.[10] The high temperatures and the gas residence times of lime kilns suggest that they are also candidates for combustion of hazardous wastes.

The kiln gases are exhausted at temperatures of 500-1400° F and generally require cooling before the gas is cleaned in the control device. Typical control devices include baghouses, ESPs, venturi scrubbers, and, occasionally, gravel bed filters.[10]

TABLE 3-2. CONTROL DEVICES ON CEMENT KILNS[a]

Process	Control device[b]	Number of kilns	Percent of total
Wet	ESP	73	51
	ESP + CS	14	9.8
	FF	27	18.9
	FF + CS	18	12.6
	Other	11	7.7
Dry	ESP	39	29.8
	ESP + CS	11	8.4
	FF	42	32.1
	FF + CS	26	19.9
	Other	13	9.9

[a]Derived from EPA's National Emissions Data Base.

[b]ESP = electrostatic precipitator
CS = centrifugal separator
FF = fabric filter

4.0 TEST RESULTS

4.1 OVERVIEW OF TESTS

Tests of waste combustion have been conducted at calcining kilns with the following features:

Process	Fuel	Control Device
Wet	Coal	ESP
Dry	Coke	Baghouse
Preheater	Fuel Oil	

The types of waste have also been quite varied and include chlorinated aliphatics, chlorinated aromatics, PCBs, chlorophenols, phenoxy acids, metal-contaminated lubricating oil, toluene, Freon 113, alcohols, and a wide variety of other organic compounds found in waste solvents. Total chlorine loads up to 9 kgCl per Mg clinker have been imposed on the kilns during waste combustion.

This section will first summarize the tests to provide general background on each specific site with respect to kiln characteristics and a general discussion of the tests. The test results are discussed collectively under the various emission categories of interest in the following sections. A summary of the tests is given in Table 4-1.

St. Lawrence Cement, Mississauga, Ontario[1,2]

Tests were performed at this Canadian plant in 1974 and again in 1975-1976.[2] The test in 1974 burned waste lubricating oils contaminated with lead and zinc and also included baseline tests without the used oil. The used oil burn was conducted in the company's dry process kiln with a 4-stage preheater. The kiln is 17 ft in diameter, 276 ft in length, and is fired with No. 6 fuel oil with exhaust gas cleaning in an ESP. A fraction of the exhaust gases is bypassed through a conditioning tower where water is sprayed into the gas to lower the temperature and to condition the gases for precipitation. The cooling and velocity reduction divide the particulate matter into two fractions: a high alkali fraction that is

TABLE 4-1. SUMMARY OF CEMENT KILN TESTS

Plant	Date	Process	APCD	Fuel	Test program					Fuel types tested
					PM	POHCs	PICs	Cl	Metals	
St. Lawrence Cement Mississauga, Ontario	1974	Dry-PH	ESP	Fuel oil	x	-	-	-	x	Lubricating oil contaminated with metals
	1975-76	Wet	ESP	Fuel oil	x	x	-	x	x	Chlorinated aliphatics (ethylene dichloride) Chlorinated aromatics (chlorotoluene) PCB's
Peerless Cement Detroit, MI	1976	Wet	ESP	Coal	-	x	-	-	-	PCB's
Slora Vika Sweden	1978	Wet	ESP	Coal	x	x	x	x	-	Chlorinated aliphatics (methylene chloride) Chlorinated aromatics (PCB 1242) Chlorophenols and phenoxy acids Freon (trichlorotrifluoroethane)
Marquette Cement Oglesby, IL	1981	Dry	ESP	Coal	x	x	-	x	x	Chlorinated aliphatics, MEK, toluene
San Juan Cement Puerto Rico	1981-82	Wet	Baghouse	Fuel oil	x	x	x	x	x	Chlorinated aliphatics
Alpha Cement Cementon, NY	1982	Wet	ESP	Coal	x	-	-	x	x	Waste solvents (Halogens = 590 ppm)
General Portland Los Robles, CA	1982	Dry	Baghouse	Coal	-	x	-	x	x	Aromatics and chlorinated aliphatics
General Portland Paulding, OH	1983	Wet	ESP	Coal	x	x	x	x	x	Chlorinated aliphatics, MEK, toluene
Lone Star Ind. Oglesby, IL	1983	Dry	ESP	Coal/coke	x	x	x	x	x	Chlorinated aliphatics, MEK, toluene
Rockwell Lime Rockwood, WI	1983	Lime	Baghouse	Coke	x	x	-	x	x	Chlorinated aliphatics, MEK, toluene

collected in the ESP and discarded and conditioning tower solids (lower alkali content) that is recycled into the raw material feed. Normally, the fuel oil is burned using three separate mechanical atomization burners. During the waste oil burn, one of the burners was used for the waste oil and the remaining two burners continued to burn No. 6 fuel oil.[1]

A second test was started on this kiln in 1975 with chlorinated aliphatics as the supplemental fuel. A buildup of solids twice occurred in the bypass duct between the kiln and the conditioning tower. Because of high particulate emissions, plugging of the bypass system, and the cost of equipment changes to correct the problems, the test of the dry kiln was terminated and switched to one of the wet process kilns at the site.[2]

Extensive tests were conducted in 1975-1976 in a wet process kiln that was 123 m (402 ft) in length and 3.5 m (11.5 ft) in diameter with a capacity of 955 Mg/day. The primary fuel is No. 6 fuel oil which is fired through a nozzle with mechanical atomization at a flow rate of 76 L/min (20 gal/min) and a pressure of 120 psi. The kiln exhaust gases are cleaned by a 6-section electrostatic precipitator (ESP) that collects 320 to 445 Mg/day of dust. Approximately 320 Mg/day of this dust is recycled to the kiln. The waste types fired included chlorinated aliphatics, chlorotoluene, and PBCs with a mixture of other chlorinated compounds. The No. 6 fuel oil is normally burned in a single burner at the center of the burner pipe. During the tests with chlorinated compounds, the waste fuel was fed through a separate pipe just above and to one side of the center with different nozzle sizes for proper atomization at different flow rates. The waste fuel was supplied with centrifugal pumps at a pressure of 120 psig. Nozzles plugging from solids was experienced during the PCB burn. On the last day of the PCB burn, the nozzle was removed to permit uninterrupted flow.[2]

Peerless Cement, Detroit, Michigan[13]

The kiln at Peerless Cement uses the wet process and is fired by coal with exhaust gas cleaning in an electrostatic precipitator. This kiln is 91-m (300 ft) in length and 4.9 m (16 ft) in diameter. Baseline (coal only) tests were conducted before and after two waste burn tests of PCBs at flow rates of 0.9 to 2.8 L/min.[13]

Stora Vika, Sweden[3,4]

This 140-m kiln uses the wet process and is fired by coal with gas cleaning in an ESP. The ESP dust is extracted with water and then recycled to the kiln with the slurry feed. A variety of chlorinated wastes were burned and included short-term tests with chlorinated aliphatics (100 hr), PCBs (24 hr), chlorophenols and phenoxy acids (12 hr), and 3 hours with Freon 113 (Trichloro-trifluoroethane). A wide range of chlorine input rates (up to 9 kgCl/Mg clinker) were used during the trial burns. Long-term tests were conducted with chlorinated aliphatics (1.5 months) and PCBs (about 1 month).[3,4]

Lone Star Industries, Oglesby, Illinois[14,15]

Two trial burns have been conducted at this kiln: one when it was formerly owned by Marquette Cement[14] and another under Lone Star, Inc.[15] The kiln uses the dry process and is fired by a coal/coke mixture. The kiln is 158 m (520 ft) in length, 4.6 m (15 ft) in diameter, and has a clinker production capacity of 1,320 Mg/day. An ESP collects about 205 Mg/day of dust and about 90 percent of it is recycled back to the kiln with the raw material feed. The two tests used waste paint solvents composed of chlorinated aliphatics, methyl ethyl ketone, and toluene. In the 1983 test, the waste fuel was spiked with Freon 113 and fired through a separate pipe under the coal pipe with pressure atomization. Total chlorine loading ranged from 1.1 to 2.2 kgCl/Mg clinker.[15]

San Juan, Puerto Rico[16]

This cement kiln uses the wet process and is fired with No. 6 fuel oil. The kiln is 137 m (450 ft) in length, 3 m (10 ft) in diameter, with a clinker production rate of 28-33 Mg/hr. The kiln exhaust gas is cleaned by a fabric filter. The waste fuel burning was part of an extensive test program from October 1981 to February 1982 by EPA.[16]

The POHCs monitored during the tests included the chlorinated aliphatic series of methylene chloride, trichloromethane, and carbon tetrachloride. The waste fuel was fired through a separate burner pipe through different nozzle diameters at a pressure of about 40 psig. The program included 5 baseline tests and 11 waste fuel tests on 7 different batches of waste fuel. The waste fuel was highly chlorinated (up to 35 percent Cl) and was burned at an average rate of 5.5 kgCl/Mg clinker.[16]

Alpha Portland Cement, Cementon, New York[17]

This kiln uses the wet process with coal as the primary fuel and gas cleaning in an ESP. The kiln clinker production rate is 45-49 Mg/hr. The tests were conducted under baseline (coal only) test conditions and also with waste solvents cofired with the coal. The emission testing focused on particulate matter, HCl, SO_2 and metals emissions for the two test conditions.[17]

General Portland, Los Robles, California[18]

The General Portland cement kiln uses the dry process and is normally fired with coal. The kiln is 171 m (560 ft) in length and has a clinker production capacity of 1,590 Mg/day. A fabric filter cleans the exhaust gas and collects 61 Mg/day of dust. About 95 percent of this dust is recycled back to the kiln. The test program included two baseline tests at different times and waste burn testing with POHCs that included methylene chloride, 1,1,1-trichloroethane, 1,3,5-trimethylbenzene, and xylene.[18]

General Portland, Paulding, Ohio[19]

The cement kiln in Paulding uses the wet process with coal as the primary fuel. The normal operation of this kiln over the past 3 years has included cofiring waste solvents as supplemental fuel. The kiln is 128 m (420 ft) in length and 3.4 m (11 ft) in diameter with a clinker production capacity of about 27 Mg/hr. A 4-field ESP is used for gas cleaning. Dust is collected at a rate of about 6.4 Mg/hr and is recycled at a rate of 3 to 4 Mg/hr. The EPA test included 4 days of baseline testing and 5 days of testing during the waste burn. The POHCs in the waste fuel included methylene chloride, 1,1,1-trichloroethane, methyl ethyl ketone, toluene, and Freon 113, which was spiked into the waste fuel. The waste fuel was fired through a separate burner pipe inside the coal burner pipe with air atomization of the solvents.[19]

Rockwell Lime, Rockwood, Wisconsin[20]

This lime kiln is 2.4 m (8 ft.) in diameter and 67.1 m (220 ft) in length and is fired normally by a mixture of coke and natural gas. Exhaust gas is cleaned by a fabric filter. The lime product is produced at a rate of about 7.7 Mg/hr. During the waste burn, the waste fuel replaced natural gas and was fed through a separate 1-inch pipe above the coke burner pipe with its nozzle pointed into the flame. The POHCs in this test were chlorinated alphatics, methyl ethyl ketone, and toluene.[20]

4.2 DESTRUCTION AND REMOVAL EFFICIENCIES (DRE) FOR PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS (POHCs)

POHCs are the hazardous constituents in the waste as defined by EPA's Appendix VIII list[21] and are selected on a case-by-case basis. Two criteria that are used include the expected difficulty of thermal degradation of the compounds and their concentrations in the waste.[22] DRE is a simple efficiency calculation based on the quantity of a compound entering the kiln with the waste and the amount emitted through the stack after thermal destruction and gas treatment in the control device. Generally, no corrections were made in the test reports summarized here for emissions of the POHC when waste is not burned (referred to as the baseline condition in this report) or for POHCs that may enter by inward leakage of ambient air or from the process water.

The concentration of the compound in the waste is an important consideration in the selection of POHCs because this concentration, the waste and air flow rate, and the detection limit of the test method determine the number of nines that can be demonstrated in the DRE calculation. Because very low (ppb) levels must be measured in the gas, EPA has developed a volatile organic sampling train (VOST) to collect nanogram (10^{-9} grams) quantities of volatile organics for analysis. From a 20-liter sample, roughly one gram-mol of stack gas is sampled (22.4 L/g-mol at standard conditions). For a total sample of 100 ng of a POHC with a molecular weight of 100, the VOST should be able to detect levels of 1 ppb by volume. If collection levels of 10 ng are distinguishable from blanks, then detection levels on the order of 0.1 ppb are possible.

Obviously, the VOST is designed to provide very low detection levels; however, contamination is introduced as an important factor that must be considered in evaluating the test data. Scrupulous care must be exercised to minimize contamination in this system in which nanograms of contaminants can create a high bias in test results. The Tenax sorbent that is used is notorious in its ability to adsorb trace quantities of organics from the air (e.g. chlorinated organics from new carpet or several types of Freon from refrigerated storage), even when the sorbent is in a "sealed" container. However, desorption or loss of compounds from the Tenax in sealed tubes has

not been documented as a problem. These factors imply that the VOST results may be biased high from contaminants, but there is no indication that the POHCs are lost by desorption in the time from sample collection to analysis. The collection of blanks and baseline samples in the cement kiln tests have been a necessary and invaluable tool in sorting out the results of POHC emission rates.

Low levels of contamination, POHCs in the ambient air, and POHCs found during baseline tests do not preclude obtaining useful and defensible results from the VOST. For example, environmentally conservative estimates of POHC concentrations can be made by assuming that all detected levels of POHCs originate from the waste and by ignoring corrections for baseline levels of contamination. If the concentration of POHC in the waste is sufficiently high and the mass collected on the sample tube is low, even if the detectable levels are caused by contamination or some other source, DREs of 99.99 percent or greater can be demonstrated. Some of the data summarized in this report falls into this category in which either low-level contamination or baseline emissions of the POHC were detected and the results still showed 99.99 percent DRE. These data will be identified and the reader should keep in mind that for these cases, DRE calculations are well bounded on the lower end and unbounded on the upper end. In other words, the DREs for these test results should be at least the measured DRE, but the actual DRE of POHCs entering only with the waste fuel may be higher.

The DRE results are summarized in Table 4-2. One of the first tests to examine the DRE of hazardous waste in cement kilns was conducted at the Canadian plant, St. Lawrence Cement. The wet-process kiln was normally fired with fuel oil and the exhaust gas was cleaned by an ESP. Three tests were conducted with batches of waste solvents labeled as chlorinated aliphatics, chlorinated aromatics, and PCBs. The chlorinated "aliphatics" were composed primarily of chloropropane, chloropropene, 1,2-dichloroethane, 1,1,2-trichloroethane, and chlorobenzene. The chlorinated aromatics batch was primarily chlorotoluene, and the waste labeled PCBs was about 50 percent PCB, 28.5 percent chlorotoluene, and a mixture of chlorinated aliphatics. Destruction efficiencies were calculated conservatively by not subtracting or correcting for the background levels from the baseline test or interferences (contamination) on the control blanks. In addition, a conservative

TABLE 4-2. SUMMARY OF DREs

Plant	Waste component	Destruction efficiency
St. Lawrence Cement	Chlorinated aliphatics	>99.990
	Chlorinated aromatics	>99.989
	PCB's	>99.986
Peerless Cement	PCB's	99.9981-99.9986
Stora Vika	Methylene chloride	>99.995
	Trichloroethylene	>99.9998
	All chlorinated hydrocarbons	>99.988
	PCB	>99.99998
	Chlorinated phenols	>99.99999
	Phenoxy acids	>99.99998
	Freon 113	>99.99986
San Juan Cement	Methylene chloride	93.292-99.997
	Trichloromethane	92.171-99.96
	Carbon tetrachloride	91.043-99.996
Los Robles	Methylene chloride	>99.99
	1,1,1-Trichloroethane	99.99
	1,3,5-Trimethylbenzene	>99.95
	Xylene	>99.99
Paulding	Methylene chloride	99.956-99.998
	Freon 113	>99.999
	Methyl ethyl ketone	99.978-99.997
	1,1,1-Trichloroethane	99.991-99.999
	Toluene	99.940-99.988
Oglesby	Methylene chloride	99.94-99.99
	Freon 113	99.999
	Methyl ethyl ketone	99.997-99.999
	1,1,1-Trichloroethane	>99.999
	Toluene	99.986-99.998
Rockwell Lime	Methylene chloride	99.9947-99.9995
	Methyl ethyl ketone	99.9992-99.9997
	1,1,1-Trichloroethane	99.9955-99.9982
	Trichloroethylene	99.997-99.9999
	Tetrachloroethylene	99.997-99.9999
	Toluene	99.995-99.998

collection efficiency of 80 percent was used. The result was a maximum estimated concentration of 50 ppb for all of the waste fuel tests, and "because of the high and uncertain background levels, the estimate is higher than the actual levels in the emissions." The DREs were based on total chlorinated organics in and out instead of analysis of specific compounds in and out. The reported DREs for wastes with mostly chlorinated organics was >99.99 percent, >99.989 percent for chlorinated aromatics, and >99.986 percent for PCB mixture.[2]

The tests at Peerless Cement used PCBs as the waste fuel at feed rates of roughly 1 and 3 qt/min. The results are summarized in Table 4-3 and show DREs of 99.9981 to 99.9986 percent. These estimates are also conservative because PCB emissions were also present during the baseline test. The river water used to make the slurry feed to the kiln contained PCBs and introduced the PCBs into the cooler (feed end) of the kiln. The test results showed no significant difference between baseline tests and tests in which PCBs were burned. An interesting observation in this test is that some of the PCBs entering the cooler end of the kiln are destroyed or removed at some point in the process other than with the stack gas. Stack emissions of PCBs were only 7 to 54 percent of the PCB entering from the river water alone.[13]

A test similar to the one conducted at St. Lawrence was conducted in Sweden at a wet process kiln in Stora Vika. Short-term tests were conducted with chlorinated aliphatics (100 hr), PCBs (24 hr), chlorophenols and phenoxy acids (12 hr) and trichlorotrifluoroethane (3 hr). Long-term tests were conducted with the chlorinated organics (1.5 months) and PCBs (about 1 month). Results are listed in Table 4-2. During both the short- and long-term tests with chlorinated aliphatics, none of the waste fuel's major components was detected in the stack gas. Based on the detection limit, the DRE of methylene chloride exceeded 99.995 percent and the DRE of trichloroethylene exceeded 99.9998 percent.[3,4]

No PCBs were detected in the stack gas during either the short- or long-term test and yielded a DRE exceeding 99.99998 percent for PCB. Similarly, no chlorophenols or phenoxy acids were detected in the stack gas with resulting DREs greater than 99.99999 and 99.99998 percent, respectively. Detectable levels of trichlorotrifluoroethane (Freon 113) were found during

TABLE 4-3. PCB TEST RESULTS FOR PEERLESS CEMENT

	Run number			
	1	3	4	5
PCB in fuel (µg/min)	0	5.66×10^8	1.7×10^9	0
PCB out (µg/min)	5,864	7,763	33,212	44,930
PCB in feed (µg/min)	8.3×10^4	6.0×10^4	7.2×10^4	8.3×10^4
DRE[a]	-	99.9986	99.9981	-

[a]Based only on PCB in fuel with no correction for baseline or for PCBs in water.

one experiment with this waste fuel and yielded a DRE of 99.99986 percent.[3,4]

The test at Los Robles on a dry process kiln included dichloromethane, 1,1,1-trichloroethane, 1,3,5-trimethylbenzene, and xylene in the waste fuel The DRE results are listed in Table 4-2. The results show a DRE of 99.99 percent or greater for 3 of the 4 compounds, and again the calculations are conservative. No corrections were made for baseline levels or for the contribution from ambient air. No trimethylbenzene was detected; therefore, the DRE for this compound is likely to have exceeded 99.95 percent.[18]

The test at Paulding, Ohio on a wet-process kiln tracked the DRE of compounds listed in Table 4-2. Again, all of the results are conservative and in this case, no corrections were made for blank contamination, baseline levels, ambient air in leakage, or the contribution from process water. Methylene chloride contamination was a problem and the DREs for this compound should be viewed as unreliably low because of the contamination. Similarly, the methyl ethyl ketone results reflect a contamination problem, although on a scale much smaller than the methylene chloride. No problems with contaminants were seen with the 1,1,1-trichloroethane and Freon 113 results which demonstrated DREs of 99.999 percent of greater.

The toluene emissions were shown to originate from coal combustion. No blank problems were experienced with toluene, baseline and waste burn emissions of toluene were the same, and the highest toluene rates occurred during a kiln upset at the baseline conditions. Benzene emission rates were also about the same for the baseline and waste fuel burn. These results were also observed during a baseline test at Los Robles with coal fuel in which both benzene and toluene were found at concentrations similar to those found at Paulding. Therefore, the calculated DRE for toluene is misleading in terms of waste destruction and a more important consideration is that toluene emissions did not increase from burning wastes that contained toluene. Even with low but steady baseline level of toluene, a DRE of 99.99 percent was reported on one test day in which the highest level of toluene entered the kiln with the waste fuel. This does not mean that an increased input rate increases the DRE; for this test, the higher DRE derives only from the mathematics of a constant small emission rate and a significantly increased input rate.[19]

The results of the test burn at Lone Star showed similar contamination problems with methylene chloride. However, the DREs for other compounds were all 99.99 percent or greater on an environmentally conservative basis, i.e., no correction for blanks, baseline, process water, or outside air. These results are based on a limited number of VOST runs because one set of samples was invalidated because of contamination. Several compounds that were not predesignated as POHCs were quantified from the Modified Method 5 sampling train. These compounds are listed in Table 4-4 and show DREs exceeding 99.99 percent.[15]

The test at Rockwell Lime burned waste fuel containing methylene chloride, methyl ethyl ketone, 1,1,1,-trichloroethane, trichloroethylene, tetrachloroethylene, and toluene. The average DRE results are listed in Table 4-2 and show an average of 99.99 percent or greater. The reported DREs are again conservative because no blank corrections were applied. DREs exceeding 99.99 percent were consistently obtained for all POHCs except methylene chloride. Three out of 28 runs averaged less than 99.99 percent for methylene chloride, but the quantity collected suggested contamination problems. The overall average DRE for methylene chloride was 99.997 percent.[20]

The test at San Juan used methylene chloride, chloroform, and carbon tetrachloride as the designated POHCs in a waste fuel with a high chlorine content (6.5-35.1 percent). This test showed a phenomenon seen at other cement kiln tests: measurable rates of the POHCs during the baseline test when no waste was burned. Blank samples showed no contamination problems; therefore, the source of the POHCs during the baseline was unexplainable. The reported DREs for this test appear to be low compared with other test results. The test report concluded that lack of atomization of the waste fuel and the difficult incinerability of highly chlorinated monocarbon compounds contributed to the low DREs. The above normal free lime content of the clinker and removal of chloride in the clinker instead of the waste dust also suggest that operating difficulties were experienced. However, the detection of POHCs during the baseline make the DRE results difficult to interpret. If the measured POHCs originated from sources other than burning waste fuel, the actual DREs may have been higher than those measured.[16]

TABLE 4-4. DREs OF COMPOUNDS FROM MM5 TRAIN AT LONE STAR

Compound	concentration in waste (g/L)	Stack emissions (µg/s)	Percent DRE
Styrene	12.5	<30	>99.999
Ehtylbenzene	11.4	<30	>99.999
O-Xylene	15.0	<30	>99.999
Benzaldehyde	18.7	236	99.998

The San Juan test, when viewed with results from other cement kiln tests, suggests that burner design, waste composition, and the kiln's operation can have a significant effect on DRE. The extent of their effect is inconclusive because of baseline POHC emissions.

4.3 POHC EMISSION RATES

POHC emission rates are summarized in Table 4-5. Because of baseline, background, and blank results that show the POHCs, these emission rates should be viewed with caution. None of the reported waste burn rates except the San Juan test were corrected for baseline emissions. The test at San Juan showed increases in POHC emission rates over the baseline for all three compounds. The test report noted that other baseline tests not included in the baseline total, which were conducted on days following a waste fuel burn, showed levels of POHCs equal to or exceeding the levels during the actual waste burn.[16] Note that the baseline emission rates at San Juan are higher than the POHC emission rates during waste combustion at other kilns. The San Juan results are difficult to interpret; however, an environmentally conservative approach would suggest significantly higher rates during the waste burn at levels exceeding those observed in any other tests.

The tests at Paulding showed no significant difference between baseline and waste burn emissions of POHCs. Note that some contamination problems were experienced with methylene chloride and methyl ethyl ketone; therefore, actual emissions of these compounds were probably lower than those reported. Coal combustion was shown to contribute to toluene emissions.[19]

The tests at Lone Star also showed methylene chloride contamination problems and low level contamination by Freon 113. Again, no significant difference was found between baseline and waste burn emission rates. The overall emission rates of POHCs are comparable (same order of magnitude) to those observed at Paulding.[15]

During the test at Stora Vika, the only compounds detected during any tests were chloroform (during the chlorinated aliphatics burn and traces during a baseline test) and Freon during that trial burn. Generally, emission rates (based on detection limits) are low and comparable to the

TABLE 4-5. SUMMARY OF POHC EMISSION RATES

Test	POHCs	Baseline emissions (mg/s)	Waste burn emissions (mg/s)
San Juan[a]	Methylene chloride	1.4	94 (<1.8 to 310)
	Chloroform	11	94 (<5.3 to 400)
	Carbon tetrachloride	71	191 (<.12 to 400)
Paulding	Methylene chloride	0.61[b]	1.1[b]
	Freon 113	<0.022	<0.025
	1,1,1-Trichloroethane	0.044	0.149
	Methyl ethyl ketone	0.77[c]	0.54[c]
	Toluene	4.7[d]	4.7[d]
Lone Star	Methylene chloride	4.8[b]	0.9[b]
	Freon 113	0.43[e]	0.075[e]
	1,1,1-Trichloroethane	<0.029	<0.014
	Methyl ethyl ketone	0.17	0.14
	Toluene	1.9[d]	0.98[d]
Stora Vika	Methylene chloride	[f]	<7.3
	Trichloroethylene	[f]	<0.3
	Chloroform	[f]	10
	PCB's	[f]	<0.04
	Chlorophenols	[f]	<0.025
	Phenoxy acids	[f]	<0.05
	Freon 113	[f]	0.03
Peerless Cement	PCB's	0.10 - 0.75	0.13 - 0.55[g]
Los Robles	Methylene chloride	<0.1 - 0.43	<0.003
	1,1,1-Trichloroethane	0.13 - 0.34	0.005
	1,3,5-Trimetnyl benzene	<0.1 - <7.6	<0.42
	Xylene	<0.1 - <3.1	<0.21
	Benzene	35 - 54[d]	76[d]
Rockwell Lime	Methylene chloride	0.0008	0.0023
	Methyl ethyl ketone	0.007	0.0105
	1,1,1-Trichloroethane	0.0048	0.0073
	Trichloroethylene	0.0027	0.0032
	Tetrachloroethylene	0.0028	0.0043
	Toluene	0.0167	0.0332

[a]Baseline results based on reported average concentration and an average gas flow of 1,800 m^3/min. Waste burn results averaged from Table 5-3 in the test report and were corrected for baseline.

[b]Results are suspect because of methylene chloride contamination on blanks.

[c]Blank values for MEK were roughly comparable to sample values; results are suspect because of potential contamination.

[d]Toluene and benzene shown to come from coal combustion.

[e]Low-level contamination of Freon 113 seen on blanks.

[f]None of the target compounds except chloroform was found during the baseline test. Emission estimates are based on detection limit values and maximum waste feed rates (except for measured values for chloroform and Freon).

[g]PCB emissions could be attributed to PCBs in the slurry water.

two preceding tests.[3,4] The PCB burn at Peerless Cement showed low levels of PCB emissions during both the baseline and PCB burn. These emissions were attributed to PCBs that entered with the river water in the slurry feed, which enters the cooler (feed) end of the kiln.[13]

The POHCs that were followed at Los Robles showed no significant difference between baseline and waste fuel tests. Benzene was found to be formed from coal combustion and cannot be fully attributed to waste combustion.[15]

The lowest POHC emission rates of any tests were found at Rockwell Lime. A fortunate aspect of this test was the lack of contamination problems and relatively clean blanks. (The only problems reported were methylene chloride contamination on 3 of 28 runs.) The methylene chloride and toluene increases over the baseline were found to be statistically significant. The differences between baseline and waste burn emission rates for the other POHCs were not significant. The emission rate results for Rockwell Lime are one to two orders of magnitude lower than the results of other tests and are several orders of magnitude lower than the San Juan results.[20]

4.4 PRODUCTS OF INCOMPLETE COMBUSTION (PICs)

The burning of complex mixtures of organic compounds can obviously yield emissions of compounds other than the POHCs. Several tests at kilns have attempted to identify and quantify both volatile (boiling point<100° C) and semivolatile organic compounds that are emitted under baseline and waste fuel test conditions. The baseline results have been particularly interesting because of the byproducts formed from coal combustion. As with the POHCs, the interpretation of the results of waste combustion on PICs are confounded somewhat by the presence of many of the same compounds during baseline tests and the potential for high bias from low level contamination or background levels.

Table 4-6 lists compounds found during the waste burn at San Juan Cement that were not found during the baseline and were attributed to waste combustion. Samples were also analyzed for polychlorinated dibenzodioxins and none were found in any sample. Trace quantities of polychlorinated dibenzofurans (Cl_5, Cl_6, Cl_7 isomers) were detected in the particulate catch from one run. However, the kiln was in an upset condition during

TABLE 4-6. PICs[a] FROM WASTE COMBUSTION AT SAN JUAN[16]

Compound	mg/hr
Benzaldehyde	10 - 18
Phenol	2.4 - 11
C_3 - alkylbenzene	3
1-phenylethanone	6.1
Benzoic acid	3.5 - 48
C_2-Benzoic acid, methyl ester	6.3
C_2-Naphthane isomers	10 - 50
C_3-Naphthane isomers	14 - 46
Anthracene	1.5 - 4.0

[a]Not detected during the baseline and considered attributable to waste combustion.

this run and the results cannot be considered representative of waste combustion. No polychlorinated dibenzofurans were detected in any other tests.[16]

The test results from Los Robles provided more insight into PICs from coal than PICs from the waste fuel. During the baseline tests, detectable quantities of benzene (120-530 ppb) and toluene (20-70 ppb) were found. Trace quantities (but above background or blank levels) of methylene chloride (0.2 ppb) and trichloroethane (0.4 ppb) were also found during the baseline test.[18]

The test at General Portland's kiln in Paulding also revealed more about byproducts from coal combustion than from waste fuel combustion. The compounds detected and emission rates are given in Table 4-7 for the baseline tests with coal as the only fuel. During the first baseline test, the kiln was in an upset condition and coal combustion was far from optimum. The compounds marked in Table 4-7 were found at concentrations during this upset condition that were significantly higher than the concentrations found during the other three baseline tests. Note that concentrations of toluene (~30 ppb) and benzene (~290 ppb) are comparable to the concentrations found during the baseline tests (coal fuel) at Los Robles. The compounds listed in Table 4-7 were found during both the baseline and waste fuel burn and no increase could be attributed to waste fuel combustion. The stack gas was also analyzed for polychlorinated dibenzodioxins and dibenzofurans. None were found at a detection limit of about 0.2 ppb by weight.[19]

During the baseline test at Lone Star with coal and coke as the primary fuel, some toluene (1.8 mg/s) and traces of C_3-, C_4-, and C_5-benzenes were found. Emission rates of biphenyl, benzaldehyde, naphthalene, and methylnaphthalenes ranged from 0.02 to 0.3 mg/s during the baseline. A small increase in emission rates was noted for a few of these compounds during the waste burn, but the overall emission rates remained in the range of 0.03 to 0.5 mg/s. No polychlorinated dibenzodioxins or dibenzofurans were found in the stack gas at a detection limit of about 0.9 ppb by weight.[15]

The majority of chlorinated organic compounds studied in the Stora Vika test were not detected in the stack gas. During an experiment with chlorinated aliphatics, some chloroform was detected (340 $\mu g/m^3$ or about 10 mg/s) at levels above that found in the background.

TABLE 4-7. POTENTIAL PICs FROM COAL COMBUSTION AT THE PAULDING TEST[19]

Compound	Emissions (mg/s)
Methyl ethyl ketone[a]	0.9
Toluene[a]	3.5
Tetrachloroethylene	0.8
Benzene[a]	36
Xylenes[a]	2.9
C_3-Benzene	5.8
C_4-Benzene	5.2
C_5-Benzene	0.7
Biphenyl[a]	2.5
Naphthalenes[a]	12.3
Methylnaphthalenes[a]	8.3

[a]These compounds exhibited emission rates during one baseline test with a kiln upset that were much higher than the emission rates during three subsequent baseline tests.

The low chloroform content of the waste entering the kiln indicated that chloroform formation was a possibility. During the burning of chlorophenols/phenoxy acids at Stora Voka, the emissions were analyzed for polychlorinated dibenzodioxins and dibenzofurans. None of the isomers with four to six chlorine atoms, which are the most poisonous, were found. In one of the experiments, a GC peak showed the same retention time as the Cl_7 and Cl_8 isomers of the dioxin and the Cl_8 isomer of the furan. However, the concentrations of the substances were too low for GC/MS analysis and the compounds' identities could not be confirmed.[3 4]

The test results for PICs have shown some minor increases from waste combustion for some tests (several compounds at San Juan and chloroform at Stora Vika). The results for coal combustion appear to be more conclusive and indicate that many of the compounds are byproducts of coal combustion. Polychlorinated dibenzodioxins and dibenzofurans have not been confirmed as PICs from waste combustion. Trace quantities were found at San Juan during kiln upset, and trace quantities may have been present when chlorophenols and phenoxy-acids were burned at Stora Vika. Tests at two other kilns[15 19] and most of the analyses at San Juan and Stora Vika revealed no detectable quantities of these compounds.

4.5 EFFECTS ON PARTICULATE MATTER EMISSIONS

The effect of waste combustion on particulate matter emissions has been of interest because the earlier cement kiln tests indicated that burning chlorinated wastes increased emissions. A review by Weitzman examined the particulate matter results when chlorinated wastes were burned at St. Lawrence Cement and Stora Vika.[11] He reported a positive correlation between chlorine input and particulate matter out of the stack, i.e., an increase in chlorine increased particulate emissions. Subsequent tests indicate that this conclusion may sometimes be true for kilns equipped with ESPs and is not necessarily true for kilns equipped with fabric filters (baghouses).

An effect on particulate emissions was predicted because chlorinated waste combustion forms HCl, which reacts with potassium, sodium, calcium, and other compounds in the kiln to form the respective chlorides. These compounds volatilize at the temperatures found at the hotter end of the kiln

and are carried to the cooler end by the hot gas.[11] Condensation in the gas phase can form a fine particulate that remains entrained in the gas. Alternatively, the compounds may condense on the kiln's walls or on particles and form a ring of solids. Ring formation may occur as repeated accumulation and loss of chlorides, or in the extreme case, as a continuing buildup which results in a large ring that impedes or stops production.

The first test at St. Lawrence Cement showed that burning waste oil contaminated with 6,000 ppm lead actually decreased particulate matter emissions. Baseline emissions of 1.1 lb/ton were reduced to 0.7 lb/ton during the oil burn. The test report authors suggested that the increased amount of water entering with the oil improved the ESP collection efficiency.[1] The test at Alpha Cement, which burned waste solvents containing 2,000 ppm lead and very low levels of chlorine, showed similar results. Baseline emissions of 1.1 lb/ton decreased to 0.8 lb/ton when the solvent was burned.[12] The control device for both of these kilns was an ESP. The primary fuel at St. Lawrence was fuel oil and at Alpha Cement the primary fuel was coal. The results from these two tests (shown in Table 4-8) suggest that burning wastes low in chlorine content may actually decrease emissions.

The tests at San Juan[16] and Rockwell Line[20] included chlorinated organics in the wastes at average levels of 5.5 and 2.7 kgCl/Mg product, respectively. The control device for these kilns was a fabric filter (baghouse). The results in Table 4-8 show no significant difference in emission rates between the baseline and waste fuel burn. Emissions were well controlled with average rates of about 0.65 and 0.25 lb/ton of product for the cement kiln and lime kiln, respectively. These test results indicate that burning chlorinated wastes does not necessarily increase emissions. No samples were taken to determine if the loading on the fabric filters increased. If the loading did increase, the baghouses were evidently adequate to remove any increased loading of particles for these two cases. (Note: The test at San Juan may not have imposed the full potential loading of chloride-laden dust on the baghouse from 5.5 kgCl/Mg clinker. A significant portion of the chloride was removed with the clinker and not with the waste dust.)

The test at Paulding was on a cement kiln with gas cleaning in an ESP. The waste contained chlorinated organics that entered the kiln at an average rate of 2.2 kgCl/Mg clinker (a range of 0.8 to 4.7 kg/Mg). The burning of

TABLE 4-8. EMISSIONS OF PARTICULATE MATTER

Plant	Test condition	Particulate matter gr/SCF	Particulate matter lb/h	Particulate matter lb/t	Cl (kg/Mg clinker) into kiln
St. Lawrence	Chlorinated aliphatics	0.21	123[a]	3[a]	4.0
	Chlorinated aromatics	0.086	45	1.1	5.5
	PCB's	0.078	44	1.1	2.5
	Baseline	0.038	21	0.5	-
	Lubricating oil	0.064	83	0.7	-
	Baseline	0.107	139	1.1	-
Marquette	Waste solvents	0.104	58	<1	1.1
	Baseline	0.093	50	<0.8	-
Alpha Cement	Solvents	0.041	44	0.8	-
	Baseline	0.050	53	1.1	-
San Juan	Wastes	0.043	22.4	0.66	5.5
	Baseline	0.041	21.7	0.64	-
Paulding	Wastes	0.030	18.9	0.65	2.2
	Baseline	0.030	19.6	0.64	0.2
Lone Star	Wastes	b	b	b	1.2
	Baseline	0.17	116	2.0	0.2
Rockwell Lime	Wastes	0.016	2.2	0.26	2.7
	Baseline	0.013	2.0	0.24	-
Stora Vika	Aliphatics	0.039	21	0.88	4.4
	Baseline	0.009	4.7	0.21	0
	PCBs	0.024	12.7	0.53	3.6
	Baseline	0.011	5.9	0.25	0
	Chlorophenols & phenoxyacids	0.058	30.9	1.36	0.95
	Baseline	0.014	7.7	0.34	0
	Freon 113	0.062	33.3	1.39	1.7
	Baseline	0.022	11.7	0.49	0

[a]Ring formation and ESP difficulties.

[b]ESP malfunctioned.

waste solvents at this kiln had been routine practice; consequently, the ESP had been adjusted for chlorinated waste combustion and the kiln's operators were experienced in cofiring waste solvents. No significant difference was found in particulate matter emissions between the baseline and waste fuel tests (~0.65 lb/ton).[19] Similarly, chlorinated wastes were burned during the Marquette Cement tests with an average chlorine input of 1.1 kg/Mg clinker. This kiln also had an ESP control device, and no significant difference was found in particulate matter emissions between the baseline and waste fuel burn. The data from these tests indicate that chlorinated wastes can be burned in a kiln with a properly operating ESP without a significant change in particulate matter emissions.[14]

More details on the potential effects of chlorinated waste combustion can be found by examining the test data collected at Stora Vika[3,4] and St. Lawrence Cement.[2] Different types of chlorinated wastes were used and the total chloride loading was varied among tests. One kiln was fired with fuel oil, the other was fired with coal, and both have an electrostatic precipitator.

The St. Lawrence results summarized in Table 4-9 show baseline emission rates of about 0.24 kg/Mg (0.48 lb/ton). When chlorinated aliphatics were burned, problems were experienced with chloride accumulation and release, which finally resulted in a kiln blockage on the last day of the test. Emissions increased to about 1 kg/Mg (2.0 lb/ton) for a level of 3-4 kgCl/Mg clinker. The highest rate (6-7 kg/Mg) resulted in a kiln blockage and upset conditions (4.6 lb/ton) followed by a kiln shutdown to remove the ring. The burning of chlorinated aromatics (primarily chlorotoluene) also yielded results (1-1.3 lb/ton) that were higher than the baseline rate. A ring also formed during this test but eventually broke away. The chloride input was roughly 4.5 to 6 kg/Mg clinker. During these two tests, a tendency toward ring formation was found in the range of 6-7 kgCl/Mg clinker. The authors noted that ring formation compounds the effect of increased total loading on the ESP because rings decrease the flow area, which increases the velocity and in turn increases the quantity of dust entrained by the gas.[2]

Emissions also increased over the baseline results when PCBs were burned, but the data do not show a significant increase in emissions as the

TABLE 4-9. SUMMARY OF PARTICULATE MATTER RESULTS AT ST. LAWRENCE CEMENT[2]

Test condition	Date	Particulate (lb/hr)	Chlorine in[a] (lb/24 hr)	Clinker out (tons/day)	kg Cl/Mg Clinker		kg particles/ Mg clinker
					Calculated[a]	Reported[b]	
Baseline	10/20/75	20.8	1,516	1,071	.71	-	0.23
	10/21/75	25.4	1,342	1,078	.62	-	0.28
	10/22/75	19.6	1,412	1,046	.67	-	0.22
	1/19/76	23.9	1,361	1,020	.67	-	0.28
	1/20/76	21.0	1,389	991	.70	-	0.25
	1/21/76	14.6	1,445	1,016	.71	-	0.12
Aliphatics	10/28/75	83.9	8,146	1,040	3.9	3.1	1.0
	10/29/75	84.6	8,604	1,021	4.2	3.2	1.0
	10/30/75	200	13,999	1,032	6.8	6.3	2.3[c]
Aromatics	12/10/75	40.3	11,791	994	5.9	4.5 - 7.1	0.49
	12/11/75	40.5	9,062	999	4.5	3.1 - 5.1	0.49
	12/12/75	55.0	12,016	1,024	5.9	7.9	0.64
PCBs	1/7/76	45.3	3,999	944	2.1	0.6 - 1.4	0.58
	1/8/76	34.5	6,413[d]	1,045	2.6	1.3 - 3.3	0.40
	1/9/76	52.2	12,348[d]	1,027	6.0	6.1	0.61

[a]Chlorine in and calculated values from the chlorine balance in the test report. Included chlorine in slurry, fuel oil, and waste fuel. These are 24 hour averages.

[b]Values reported by authors in summary, apparently for chlorine from waste fuel. Ranges reflect variations in flow rate within the test day.

[c]Ring formation in kiln terminated the test.

[d]Waste was burned 24 hours per day except for this test day which was only 735 minutes. Chlorine in was adjusted for waste fuel to reflect a 24-hour rate.

chlorine loading increased from about 2 to 6 kgCl/Mg clinker. The data show that the combustion of chlorinated aliphatics increases emissions for chlorine levels of 2-7 kgCl/Mg clinker. The results for chlorotoluene and PCB show a two-fold increase over baseline for a wide range of chloride loadings (2.1 to 6 kg/Mg). The aliphatics apparently caused a four-fold increase with chloride loadings of 3-4 kg/Cl/Mg clinker. It is likely that the increased emissions are at least partially attributable to a change in the dust resistivity from an increased alkali content. The test report notes that in the design of the precipitator could compensate for this change.[2]

The emission rates for St. Lawrence (neglecting the kiln upset) are not significantly different from the overall performance of other kilns. Note that a baseline test on a dry kiln at St. Lawrence yielded an emission rate (1.1 lb/ton) that was about the same as those from the wet kiln burning chlorinated wastes (1.1, 1.1, and 2 lb/ton). The particulate emission rates at St. Lawrence did not significantly add to the suspended particulate matter in the ambient air around the plant.

The Stora Vika tests were also conducted with various types of wastes and varying levels of chloride input. Short-term tests were conducted with chlorinated aliphatics (100 hr), PCBs (24 hr), chlorophenols and phenoxy acids (12 hr) and trichlorotrifluoroethane (3 hr). Long-term tests were conducted with the chlorinated aliphatics (1.5 months) and PCBs (about 1 month). Results for particulate matter are summarized in Table 4-10.[3]

The baseline tests at Stora Vika yielded results that ranged from 0.10 to 0.24 kg/Mg (0.2-0.48 lb/ton) and indicates a fairly well-controlled kiln when compared with the emissions data in Table 4-8. The burning of chlorinated aliphatics with chloride inputs of about 4 to 8 kg/Mg clinker increased emissions by a factor of 3 to 4 to 0.4-0.5 kg/Mg (0.8 to 1.0 lb/ton). The burning of PCBs also increased emissions; however, the increase was not significant for chloride loadings of about 3 kg/Mg and showed an increase comparable to the aliphatics (1 lb/ton) for a chloride loading of 5.6 kgCl/Mg clinker.[3]

The results for the phenoxy acids/chlorophenols and Freon are less easily explained in terms of chloride. Significant increases (to about 1.4 lb/ton) were observed for both types of waste fuel. However, the

TABLE 4-10. PARTICULATE MATTER RESULTS FOR STORA VIKA[3,4]

Waste fuel	Rate (L/min)	Chlorine in (kg/hr)	Clinker out (Mg/hr)	kg Cl per Mg clinker	Particulate (kg/hr)	Emissions (kg/Mg)
Chlorinated aliphatics[a]	395	85	21.6	3.9	9.4	0.44
	580	125	21.5	5.8	11.1	0.52
	580	125	21.8	5.7	8.1	0.37
Baseline test	--	--	--	--	2.1	0.10
PCBs[b]	360	68	21.6	3.1	4.0	0.19
	640	121	21.6	5.6	10.8	0.50
	360	68	21.6	3.1	2.6	0.12
Baseline test	--	--	--	--	2.7	0.13
Phenoxy acids[c] and chloro-phenols	980	21.6	20.7	1.0	15.3	0.74
	980	21.6	20.7	1.0	14.1	0.68
	980	21.6	20.7	1.0	12.8	0.62
Baseline test	--	--	--	--	3.5	0.17
Freon 113[d]	85[e]	48	21.8	2.2	--	--
	58[e]	33	21.8	1.5	15.2	0.70
	59[e]	34	21.8	1.6	15.0	0.69
Baseline test	--	--	--	--	5.3	0.24
Chlorinated aliphatics[f]	--	--	--	4 to 7.9	10.7	0.51
Baseline	--	--	--	--	2.1	0.10

[a]Contained an average of 24 percent Cl. Assumed specific gravity of 0.9.

[b]Contained an average of 15.7 percent Cl. Assumed specific gravity of 1.2.

[c]Contained an estimated 22 g Cl/L.

[d]Contained an estimated 57 percent Cl.

[e]These rates are in kg/hr.

[f]Results from a long term test.

chloride loading was low and ranged from 1 to 2 kg/Mg clinker. Note that the baseline tests during these two experiments showed emission levels of about 0.4 lb/ton compared to about 0.2 lb/ton for the other baseline tests. It is difficult to conclude if this is a natural variation in test results or attributable to some change in the process or ESP.

The tests at Stora Vika showed that, for the chlorinated aliphatics and PCBs, the increased chloride loading increased emissions. The total emissions reached a maximum of about 1 lb/ton and are comparable to other cement kiln test results. The burning of the chlorophenols/phenoxy acids and Freon also increased emissions over the baseline by a factor of roughly 3 (to 1.4 lb/ton). Long-term tests with chlorinated alpihatics and PCBs confirmed the increase for these types of compounds at chloride loadings of 4.0-7.9 kg/Mg for the aliphatics and 6.2 kg/Mg for the PCBs.[4]
The test data collected to date show similar results for pairs of tests:

- The testing of two kilns equipped with baghouses (San Juan and Rockwell Lime) showed no increase in particulate matter emissions when chlorinated wastes were burned.

- The testing of two kilns equipped with ESPs (St. Lawrence Cement's dry process kiln and Alpha Cement) showed a decrease in emissions when wastes were burned that were low in chlorine content.

- The testing of two kilns equipped with ESPs (Paulding and Marquette) showed no change in particulate matter emissions when chlorinated wastes were burned at rates of 1.1-4.7 kgCl/Mg clinker.

- The testing of two kilns equipped with ESPs (St. Lawrence's wet process kiln and Stora Vika) yielded results for different wastes and different chlorine loadings. Emissions were positively correlated with chlorine loading; however, the extent of the increase in emissions was different for different compounds and different kilns. Chloride accumulation, as evidenced by ring formation and subsequent release or pluggage, begins to occur in the range of 6-9 kgCl/Mg clinker.

Although increased chlorine loading at the St. Lawrence and Stora Vika kilns increased particulate matter emissions, there was no known attempt to compensate for changes in the dust's resistivity. The tendency to form chloride rings during high chlorine loading provides an incentive to the kiln's operator to limit the chlorine entering the kiln. Limiting the

chlorine may avoid plugging and process disruptions as well as limiting the chloride dust loading on the ESP. The test data suggest that particulate matter emissions from chlorinated waste combustion are controllable by a properly-operating control device and a reasonable limit on chloride loading to avoid ring formation and excessive dust loading. Adjustments may be required on a site-by-site basis to optimize ESP performance to account for changes in the dust resistivity.

4.6 FATE OF CHLORINE

Burning chlorinated wastes in cement kilns can significantly increase the chloride loading in the process. Several studies have focused on the fate of the chlorine and effects on waste dust composition and generation rate, emissions of particulate matter, and emissions of HCl.

The effects of additional chloride in cement kilns was known by kiln operators before the recent test programs of chlorinated waste combustion. It has been common practice in the cement industry to add chlorides such as calcium chloride or waste hydrochloric acid to the raw material feed to reduce alkalis.[23] The term "alkalis" refers to potassium oxide (K_2O) and sodium oxide (Na_2O) which are frequently combined and expressed as equivalent Na_2O. The concentrations of the two alkalis in the raw meal vary by source of the raw material. An alkali specification on the cement of 0.6 percent (as equivalent Na_2O) is used in North America because alkali reactive aggregates (containing geologically young amorphous silica and some dolomites) are used in many areas. These reactive aggregates cause expansion and disruption of concrete made from cement with a high alkali content. Non-reactive aggregates have been found to perform well with cement independent of alkali content.[2 23] One report also states that strength and settling characteristics are also related to the alkali concentration in the cement kiln.[2] Consequently, the alkali content is a specification that must be dealt with by the operators.

When chlorinated wastes are burned, the temperatures in the kiln favor the complete conversion of chloride in the waste to HCl. The HCl is rapidly absorbed by the calcium, sodium, and potassium oxide in the kiln's solids and converted to the respective calcium, sodium, and potassium chlorides. The resultant potassium and sodium chlorides are vaporized by the temperatures

at the hot end of the kiln, travel down the length of the kiln, and begin to condense on cooler surfaces or in the gas.[11] Figure 4-1 shows a chloride cycle that is developed in the kiln and dust collection system. Note that chlorides are removed with the dust in the cyclones and final gas cleaning device. It is a routine practice to recycle the majority of this collected dust back to the kiln, either with the raw material feed or by additions near the firing end of the kiln. The second figure shows how the chloride cycle is shifted and the chloride content of the clinker is decreased by removing or bypassing some of the collected dust. This dust is removed and disposed of instead of being reintroduced into the kiln and provides one mechanism of control for the chloride cycle. Note that by increasing the amount of dust wasted from the cyclone, the chloride dust loading on the final gas cleaning device can actually be decreased.[23] Disposal of a portion of the waste dust has been a common practice, and several kilns burning chlorinated wastes have increased their dust disposal rate (decreased their percent recycled) to control the chloride cycle.

These chlorides also condense on the kiln walls and can create rings of solids. As the kiln rotates, solids tumble from the wall and the newly-exposed wall is cooler than the gas or surface solids.[24] The rotation of the wall and exposure of cooler wall surfaces as the solids are removed appears to promote ring formation. The chloride deposites can remain sticky at the kiln's temperatures, and when the chloride loading remains too high, the deposits begin to accumulate. Sulfur can be a similar bad actor in the buildup of solids. Alkali sulfates, because of their higher melting points, tend to end up in the clinker. However, when there is an excess of sulfur to alkali, calcium sulfate forms. These sulfates start out soft and easy to remove but can become hard and difficult to remove with time. The hardening has been found to be especially pronounced when chlorides are present.[23]

The chloride cycle is affected by many factors such as chloride loading, alkali content, dust recycle rates, and temperatures. In addition, kilns also exhibit nonequilibrium behavior patterns for alkalis and sulfur. Competition for absorption may also exist between the acidic HCl and SO_2 gases. These factors tend to confound attempts at describing a precise behavior pattern of chloride and sulfates that would be applicable to kilns

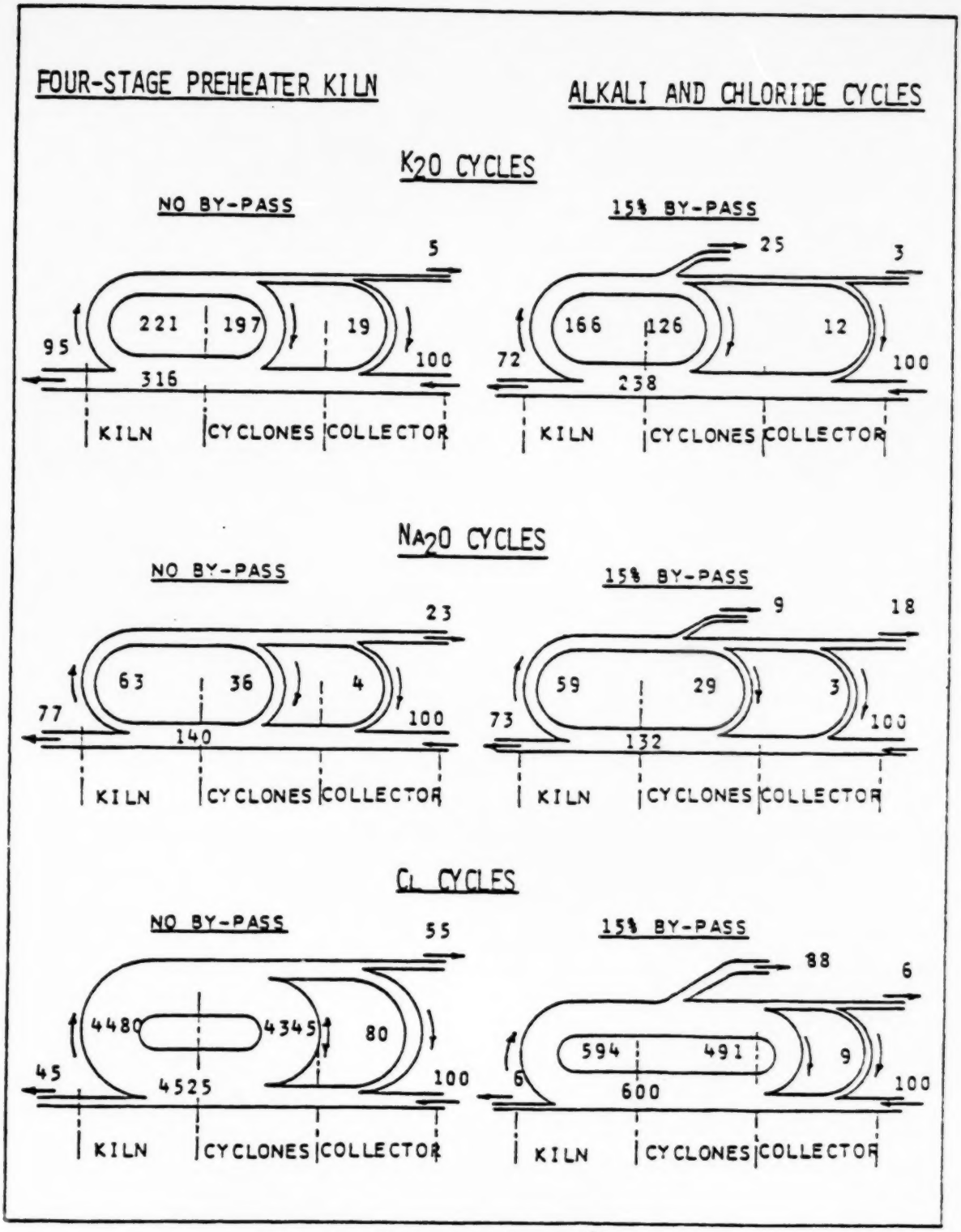

Figure 4-1. Alkali and chloride cycles[23].

in general. Site specific factors such as chloride loading, alkali content, temperature control, operating conditions, etc. all effect the chloride and sulfate cycles. Consequently, the emission test results reveal varying levels of HCl emissions, SO_2 emissions, percent chloride in the clinker, and varying effects on particulate matter emissions. The variability exists not only among different kilns, but also at the same kiln over time.

Another issue relates to the combustion of chlorinated organics that are contaminated with metals such as lead and zinc. The formation of volatile chlorides such as lead chloride (boiling point of 501° C) and zinc chloride (boiling point of 732° C) suggested to many the possibility of increased metal's emissions.[8] The fate and distribution of metals entering with the waste fuels have been tracked in several tests and are discussed in Section 4.7.

HCl emission results are listed in Table 4-11. In the test at Alpha Cement, waste solvents were burned that contained 590 ppm of identified organic halogens; total chlorine content was not reported. HCl emissions during the baseline test averaged 2.4 lb/hr (1.6-3.6 lb/hr) compared to an average of 5.8 lb/hr (4.2-7.3 lb/hr) during the solvent burn. The chloride content of the dust was about 1.5 percent for both test conditions.[17] There are not enough data to estimate the kiln's chloride removal efficiency. The data do show an increase in HCl emissions from burning the waste solvents.

The test at Marquette Cement showed HCl emissions to be higher during the baseline than during the waste burn (190 vs. 115 lb/hr). The waste contained an average of 4.5 percent chlorine and entered the kiln at an estimated rate of 1.1 kgCl/Mg clinker. These data suggest that the additional chloride entering the kiln with the waste fuel was removed in the kiln's process solids. However, the emission rate for HCl was much higher for this kiln during the baseline than the other kilns listed in Table 4-11. Similarly, SO_2 emissions were higher during the baseline than during the waste burn (57 vs. 18 lb/hr). The change in SO_2 is more than can be accounted for by the substitution for 11 to 14 percent of the sulfur containing coal by low-sulfur waste fuel. Higher levels of hydrocarbons, SO_2, NO_x, and HCl were found during the baseline test but unstable operating conditions contributed considerable variability within the data sets. At the

TABLE 4-11. HCl EMISSIONS

Test	Condition[a]	HCl (lb/h)	HCl (lb/t)	Notes
Alpha Cement	W	5.8	0.11	Organic halogens in fuel = 590 ppm
	B	2.4	0.05	
Marquette	W	115	1.9	Avg. 1.1 kgCl/Mg clinker for waste burn; waste avg.= 4.5% Cl
	B	190	3.2	
San Juan	W	0.79	0.02	Avg. 5.5 kgCl/Mg clinker for waste burn; Waste avg. = 6.5 - 35.1% Cl
	B	<0.19	<0.06	
Los Robles	W	1.03	0.015	Waste = 2% Cl; Avg. 1.1 kgCl/Mg clinker
	B	0.55	0.007	
Paulding	W	4.62	0.16	Avg. 2.2 kgCl/Mg clinker; Waste avg. = 2% Cl
	B	1.25	0.04	
Lone Star	W	25.3	0.46	Avg. 1.2 kgCl/Mg clinker; Waste avg. = 1.9% Cl
	B	2.9	0.054	
St. Lawrence	W	<1	<0.02	6.8 kgCl/Mg clinker, max. 0.7 kgCl/Mg clinker for baseline
	B	<1	<0.02	
Rockwell Lime	W	0.44	0.05	Avg. 2.7 kgCl/Mg lime; Waste avg. = 3.1% Cl
	B	0.20	0.02	

[a] W = waste burn
B = baseline

95-percent confidence level, no significant increase was noted between waste fuel and baseline emissions of HCl, NO_x, and SO_2.[14]

During the San Juan test, highly-chlorinated solvents (up to 35.1 percent chlorine) were burned at an average rate of 5.5 kgCl/Mg clinker. The average chloride input from the waste averaged 351 lb/hr and stack emissions of HCl were less than 0.8 lb/hr. HCl emissions increased during the solvent burn, but the kiln removed well over 99 percent of the potential HCl. Most of the additional chloride was removed in the clinker (average of 308 lb/hr); only marginal and sporadic increases in chloride concentration were seen in the waste dust.[16] These data indicate that the chloride cycle in this kiln was different from those of other kilns tested. Other tests show most of the chloride is removed with the waste dust.

During the test at Los Robles, an average of 160 lb/hr of chlorine entered the kiln and stack emissions of HCl were about 1 lb/hr. This kiln also removed over 99 percent of the potential HCl emissions in the process solids. An increase in HCl emissions over the baseline results was observed.[18]

In the test at Paulding, the average chlorine from the waste was 12.3 lb/hr and the average HCl emissions were 4.6 lb/hr. The results are summarized in Table 4-12 and show that ten percent of the chloride escaped as HCl during the baseline compared to about 5 percent during the waste burn. HCl emissions increase as the chloride loading from the fuel increases, but 95 percent or more of the chloride is retained in the process solids. Most of the additional chloride was retained by the waste dust, and from Table 4-12, the chloride concentration of the waste dust increases as the chlorine input increases. One exception was on the first day of waste fuel testing (Test Run 5) when detectable levels of chloride appeared in the clinker (as in the San Juan test). During this run, about 41 percent of the chloride was removed with the clinker and only 59 percent with the dust. The HCl results in Table 4-12 also show for that run the lowest rate of HCl emissions, which were one-half the average baseline rate.[19] Evidently the chloride cycle shifted in this kiln from burning the chlorinated wastes. It is also possible that an equilibrium chloride cycle had not been established although over 40 hours of waste burning was conducted before starting the test.

TABLE 4-12. HCl RESULTS FOR THE PAULDING KILN[19]

Test run	Chlorinein fuel (kg/hr)	HCl emissions (kg/hr)	Waste dust (percent Cl)
Baseline[a]	6	0.6	0.15
5	32	0.3	0.70
6	21	1.0	0.70
7	41	1.5	0.67
8	72	2.3	1.01
9	128	5.4	1.73

[a]Average of four runs.

The test results for Lone Star are given in Table 4-13. For most runs, approximately 90-97 percent of the chlorine was removed with the process solids. The chloride concentration of both the recycle dust and waste dust increased during the waste fuel burn. The results for Test 5 at the same chloride input rate as the previous test showed some interesting results. HCl emissions increased dramatically (confirmed by 2 HCl runs) and the chloride concentration of both the waste dust and recycled dust continued to increase.[15] This also indicates a shift in the chloride cycle, but in the opposite direction of the shift at San Juan and Test Run 5 at Paulding. In those cases, the cycle shifted toward the clinker end of the kiln with chloride removal by the clinker, whereas the shift here was toward the cooler end of the kiln with an increasing amount of chloride in the dust and stack gas. This test indicated that a kiln can retain chloride from the waste fuel in the process solids, but the efficiency can vary. (There is also a possibility that if any fine chloride particles escaped through the sampling filter, then they would have been measured as HCl in the impinger solution).

During the test at St. Lawrence Cement, highly chlorinated solvents were burned at rates up to 6.8 kgCl/Mg clinker (571 lb/hr chlorine). HCl emissions were less than 1 lb/hr during both the baseline and solvent burns. The kiln was very efficient at retaining chloride in the process solids (over 99 percent). The excess chloride was removed with the waste dust and no detectable levels of chloride were found in the clinker. The chloride concentration in the waste dust increased, and the dust discard rate was increased by the kiln's operator.[2] This test indicates that the operator's may control the chloride cycle in the kiln by changing the waste dust discard rate. This discard rate was increased to an apparent advantage in this kiln. However, an optimized adjustment in the dust discard rate is likely to require case by case study because of variations in chlorine input, alkali content, kiln design, kiln operating conditions, etc.

The test at Rockwell Lime burned chlorinated wastes at only 0.8 lb/hr. Most of the chlorine entered the kiln with the slurry feed (40-50 lb/hr). A small but statistically significant increase in HCl emissions was noted when waste fuel was burned. However, the chloride material balance showed that over 95 percent of the total chloride entering the kiln was retained in the process solids.[20]

TABLE 4-13. HCl TEST RESULTS FOR LONE STAR[15]

Test	Chlorinein fuel (kg/hr)	HCl emissions (kg/hr)	Recycle dust (% Cl)	Waste dust (% Cl)
Baseline	10	1.3	0.72	3.5
3	60	2.2	1.3	5.7
4	71	5.5	1.4	6.1
5	72	26.7	1.9	8.1

In summary, burning chlorinated wastes appears to increase HCl emissions. However, the vast majority of the additional chloride entering the kiln is retained in the process solids (generally 90 to over 99 percent). The chloride is usually removed with the waste dust. In some rare cases, there is an apparent shift in the chloride cycle and the extra chlorine appears in the clinker. Increasing the waste discard rate appears to be necessary when chlorinated organics are burned. These test results indicate that more study may be needed, perhaps on a case by case basis, to optimize the chloride cycle. The advantages to the kiln's operator to optimize this cycle include minimizing ring formation, HCl emissions, chloride in the clinker, and optimizing the waste dust loading on the final gas cleaning device.

4.7 EFFECTS ON LEAD EMISSIONS AND REMOVAL BY PROCESS SOLIDS

The distribution of metals has been examined in several cement kiln tests to track the fate of metals found in the waste fuels at concentration levels ranging from <100 ppm to 6,000 ppm. The effect of chlorine on metal's distribution has been of particular interest because of the potential for forming volatile metal chlorides, which could increase the loading on the gas cleaning device. Table 4-14 lists the boiling points of several compounds that could be present in the kiln's dust. The lead and zinc halides boil well below the kiln's maximum temperatures; consequently, volatilization of these compounds is likely.

At Saint Lawrence cement, waste lubricating oil was burned in a dry process (preheated) cement kiln. The oil contained an average of 0.6 percent lead and 0.15 percent bromine. Lead was added to the kiln at an average rate of 37 lb/hr during the waste oil burn with a corresponding emission rate in the stack gas of 0.013 lb/hr. However, two baseline tests yielded even higher emission rates of 0.015 and 0.023 lb/hr; therefore, the burning of waste lubricating oil appeared to decrease lead emissions. The lead entering the kiln was distributed primarily in the clinker (75-85 percent) with the balance in the conditioning tower solids (9 percent) and bypass dust (4 percent). Lead concentrations in the clinker ranged from 0.0014-0.0070 percent with a maximun of 0.013 percent. These lead levels had no adverse effects on cement quality. The authors concluded that

TABLE 4-14. BOILING POINTS OF SELECTED COMPOUNDS[25]

Compound	Boiling point (°C)
$PbBr_2$	918
$PbCl_2$	954
PbO	1472
Pb	1744
$ZnBr_2$	650
$ZnCl_2$	732
Zn	907
KBr	1383
KCl	1407
NaBr	1392
NaCl	1465

finding most of the lead in the clinker suggested that the lead must be either oxidized or taken into solid solution in the clinker.[1]

A subsequent test on a wet process cement kiln at St. Lawrence burning chlorinated solvents showed lead concentrations of 0.04 mg/m^3 in the stack gas for the baseline and for burning chlorinated aromatics. During the PCB burn, an average concentration of 0.12 mg/m^3 was reported. The increase in lead concentration corresponds roughly to the increase in concentration of total particulate matter. Baseline emissions of 21 lb/hr of particles increased to about 44 lb/hr during the PCB burn. Based on an average gas flow of 2,300 standard m^3/min, the lead emission rates ranged from 1.5 to 4.6 mg/s. The lead content of the waste solvents was very low and ranged from 0.3 to 0.8 ppm.[2]

The test at Alpha Cement used waste solvents containing about 2,000 ppm lead. The particulate catch contained about 650 ppm lead during the baseline compared to 3,000 ppm during the wast burn. These concentrations and the reported particulate matter rates yield an estimate of about 17 mg/s for the waste burn and 4 mg/s for the baseline.[17]

The test at Marquette Cement burned waste solvents that contained 1,000 to 2,500 ppm lead, 900-1,800 ppm zinc, and 450-725 ppm chromium. A comparison of average results is given below:

	Metal's Emissions (mg/s)		
	Pb	Zn	Cr
Baseline	5.0	0.3	2.5
Waste burn	9.1	2.3	6.7

Although the average results show an increase, the values for individual runs were quite variable for the two test conditions.[14]

The test at Los Robles burned fuel containing 134-739 ppm lead which was fed at a rate of 0.8 to 4.9 lb/hr. The quantity of particulate matter captured after gas cleaning in the baghouse was too small for metal's determination. The lead content of the baghouse dust increased from 750 ppm during the baseline to about 1,330 ppm during the waste burn.[18]

Waste fuel at the Paulding, Ohio site contained 149 to 814 ppm lead and 246 to 744 ppm zinc. The total lead entering the kiln averaged about 14 lb/hr during the waste burn compared to about 7 lb/hr (primarily from the slurry feed) during the baseline. Lead emissions during the baseline

averaged 1.5 mg/s compared to 6.9 mg/s during the waste burn. A shift in the lead distribution was noticed as the precipitator dust increased in lead concentration from 395 to 1,530 ppm. No increase in the lead concentration of the clinker was noted with values of 66 to 143 ppm lead reported.[19]

At the Lone Star test, the waste fuel contained 600 to 1700 ppm lead. An ESP malfunction prevented useful emission results from being determined. During the baseline, the clinker's average concentration of lead was 5.7 ppm compared to 35 ppm during the waste burn. The lead concentration in the waste dust increased from 116 to 2,650 ppm. During the baseline, the clinker removed 77 percent of the lead, whereas the majority of the lead (58 percent) was removed with the waste dust during the waste burn.[15]

The waste fuel burned at the Rockwell Lime test contained low levels (~130 ppm) of lead. No lead was detected in the lime product, and the concentration in the baghouse dust increased from below the detection limit (~28 ppm) to an average of 230 ppm. Stack emissions of lead were not detectable during the baseline test; an emission rate of about 1.7 g/hr was reported during the waste fuel burn.[20]

The emission results for lead are listed in Table 4-15. For comparison purposes and added perspective, the lead emission rates are compared with the emissions from an automobile that burns lead fuel.[26] The comparison suggests that lead emissions from the kiln, whether waste fuel is burned or not, are about the same order of magnitude as the emissions from one to several automobiles burning leaded fuel.

The first St. Lawrence test indicates that most of the lead is retained in the process solids with no increase (actually a decrease) in stack emissions when waste fuel containing lead was burned. This test included a high concentration of lead and a low concentration of halogens in the waste fuel. The second test at St. Lawrence included a fuel that was much higher in halogen content and a very low lead concentration. These data do not show a significant increase in lead emissions from burning the wastes, except for the PCB burn in which total particle emissions increased correspondingly.

The results for Alpha Cement, Marquette, and Paulding indicate that when wastes containing 1,000 to 2,000 ppm lead are burned, lead emissions

TABLE 4-15. SUMMARY OF LEAD EMISSIONS

Test	Waste fuel	Condition[a]	Pb emissions (mg/s)	Notes
St. Lawrence	Lubricating oil	B	2-3	6,000 ppm in waste; Pb retained in process solids
		W	2	
St. Lawrence	Cl aromatics	W	~1.5	0.3 to 0.8 ppm in waste; Pb in waste dust increased
	PCB's	W	~4.6	
	Baseline	B	~1.5	
Alpha Cement	Waste solvents	B	~4	2,000 ppm in waste; Pb in waste dust increased
		W	~17	
Marquette	Cl solvents	B	5	1,000 to 2,500 ppm in waste; Pb in waste dust increased
		W	9	
Paulding	Cl solvents	B	1.5	149-814 ppm in waste; Pb in waste dust increased
		W	6.9	
Los Robles	Cl solvents	B	(b)	134-739 ppm in waste; Pb in waste dust increased
		W	(b)	
Rockwell Lime	Cl solvents	B	<0.42	130 ppm in waste dust; Pb in waste dust increased
		W	0.47	

[a] B = baseline
W = waste fuel burn

[b] Total particle emissions too low for determination.

can increase. However, the tests also show that most of the lead entering the kiln is retained in the process solids. The lead in the waste fuel and perhaps the chlorine content of the fuel appear to shift the distribution of lead such that more is removed with the waste dust.

In conclusion, the cement kiln has a large potential for retaining lead from waste fuel in the process solids. The various tests suggest that lead can be retained in the clinker with no adverse effects on clinker quality. When chlorinated wastes are burned, the data suggest that the lead is still retained in the process solids, but more of it appears in the waste dust. These test results show that, with a high lead loading and with chlorinated solvents, lead chloride is formed and removed by the ESP or baghouse. Emission estimates also show that burning lead-containing fuels increases lead emission rates. Although the percent increase in lead emissions may appear high for some tests (a factor of roughly 2 to 4), a more important point is the absolute impact of total emissions. As shown in Table 4-15, the lead emission rates for all tests but one were below 10 mg/s and are roughly comparable to emissions from automobiles burning leaded gas.

Another perspective is to consider that when waste oil is burned in boilers, 50 to 60 percent of the lead from the oil is emitted.[1,27] Much more lead is emitted during soot blowing. In contrast, the cement kiln can retain well over 99 percent of the lead in the process solids.

4.8 EFFECTS OF WASTE COMBUSTION ON NO_x and SO_2 EMISSIONS

The tests of several kilns have followed the effects of waste combustion on NO_x and SO_2 emissions and the results have been quite variable from kiln to kiln. The alkaline materials in the kiln scrub SO_2 from the gases at efficiences that vary because of the sulfur content of the primary fuel, alkali content of the raw materials, HCl in the gas, O_2 input, waste replacement rate, etc.

NO_x emissions are also quite variable and range from 200 to 1,500 ppm within hours at the same kiln. A discussion by Peters and Mournighan (26) explain that in the kilns, a direct relationship exists between NO_x emissions and secondary air (heated air from the clinker cooler) with little NO_x found from the nitrogen in the fuel. Kilns are generally operated as

"poor" combustors compared to boilers because of a reduced primary air/fuel mix, poor secondary air mixing, and generally a confined, narrow flame configuration. Excess air and its temperature are the main determinants in kiln NO_x emissions.[28] This implies that NO_x concentrations are very dependent upon the specific operating conditions of a given kiln and are not likely to be affected by waste burning.

KVB, Inc. has investigated the effects of different process parameters on NO_x emissions in a pilot scale rotary cement kiln fired by natural gas and coal. Their study found that increases in either kiln exit oxygen or the secondary air temperature increased NO emissions. The empirical relationships developed for the kiln they studied were:

Gas fuel: $NO(ppm) = 87.7 + 45.3(O_2\%) + 0.16(T_s\ ^\circ F)$

Coal fuel: $NO(ppm) = -164.6 + 77.2(O_2\%) + 0.67\ (T_s\ ^\circ F)$

These results predict a 45-77 ppm decrease in NO emissions from a 1 percent decrease in the kiln exit O_2. The effect of secondary air temperature appears to be more pronounced for coal. A decrease of 100° F in secondary air temperature yields a 67 ppm decrease in NO for coal compared to a 16 ppm decrease for gas fuel.[28]

The effect of the primary/secondary air ratio was also examined. The results for natural gas firing showed that NO emissions peaked at a primary air concentration of 20 percent and decreased at higher and lower ratios. A similar result was found for coal fuel where NO emissions peaked at about 23 percent primary air. The report explained that at primary/secondary air ratios less than the peak (0.20-0.23), flame intensity (mixing) was less and resulted in lower NO. For the higher ratios, the higher mixing is overshadowed by the larger amount of cold air introduced into the flame zone.[28]

NO emissions were also found to increase with increases in secondary air temperature. For example, increasing the secondary air temperature from ambient to 900-1100° F doubled NO concentrations. The report concluded that combustion modifications can be effective in reducing NO_x emissions. The report did not discuss the effects on SO_2 emissions or the effects on product quality (although they attempted to make "good" clinker during the test runs).[28]

SO_2 emission test results are summarized in Table 4-16. The results show that substitution of the sulfur-containing primary fuel with a low sulfur waste fuel decreased SO_2 emissions in tests at Alpha Cement, Marquette Cement, and General Portland at Paulding. At Paulding, the kiln's process solids retained about 60 percent of the total sulfur during both the waste burn and baseline tests. The San Juan test showed an increase in SO_2 emissions when waste fuel was burned. The increase was attributed to a lower O_2 input (as evidenced by lower NO_x emissions) and competitive acid gas scrubbing from HCl in a relatively low alkaline kiln when burning the highly chlorinated wastes (average of 5.5 kgCl/Mg clinker).

At Los Robles average SO_2 concentrations were relatively low (27 ppm) as was the sulfur content of the coal (0.43 percent). Sulfur removal in this kiln averaged 89 percent. NO_x emissions appeared to decrease when the waste was burned, but the decrease (see Table 4-17) was not statistically significant when the variance between runs is considered. At Los Robles, a steady decrease in NO_x emissions on one test day from 1054 to 526 ppm was attributed to a decrease in kiln excess air from 1.3 to 0.5 percent O_2. The somewhat lower NO_x during the waste burn and one baseline test was atrributed to additional chains that were installed to improve heat transfer from the gas to the incoming feed. The more efficient use of heat permitted the firing end of the kiln to be operated at lower temperatures with a resultant reduction in NO_x.[18]

The test at Lone Star showed relatively low SO_2 concentrations that ranged from about 2 to 38 ppm. Although the average results indicate an increase in SO_2 emissions when wastes are burned, two of three waste fuel tests results for SO_2 were about the same as the baseline results. The highest SO_2 concentrations were seen during the third waste burn test which averaged 38 ppm SO_2 with an exit O_2 of 6.7 percent. For the two subsequent test days, the kilns exit oxygen was increased to 7.3 and 7.5 percent, respectively, with resultant decreases of SO_2 to 13 and 5 ppm, respectively. NO_x concentrations during the baseline were lower than during the waste burn (620 vs. 814 ppm) and can probably be attributed to the lower O_2 input for the baseline (average 6.5 vs. 7.2 percent O_2). The variation of NO_x with secondary air flow was demonstrated by oscillations in undergrate pressure. Increases in undergrate pressure yielded increased NO_x concentrations and periodic fluctuations of 100 ppm or more were observed.[15]

TABLE 4-16. SUMMARY OF SO_2 EMISSIONS

Test	Condition	SO_2 (lb/h)	SO_2 (lb/t)	SO_2 (ppm)	
Alpha Cement	W	58.5	1.1	33	S in coal = 2.6%; S in waste = 0.2%
	B	138	2.7	78	S during waste burn = 2.0%
Marquette	W	11.5	0.19	18	S in waste = 0.08%
	B	57.1	0.95	93	S in coal = ?
San Juan	W	264	8	450	S in fuel oil = 2.15%
	B	170	5	279	
Los Robles	W	21.7	0.36	27	S in coal = 0.43%
	B	23.7	0.38	27	
Paulding	W	207	6.8	265	S in coal = 4.3%
	B	526	17.2	636	
Lone Star	W	14.7	.12	19	S in coal/coke = 2.7%
	B	5.6	.10	7	
Rockwell Lime	W	97	11.4	596	S in coke = 4.1%
	B	149	17.5	553	

TABLE 4-17. SUMMARY OF NO_x EMISSIONS

Test	Condition[a]	NO_x (lb/h)	NO_x (lb/t)	NO_x (ppm)
Marquette	W	275	4.6	544
	B	404	6.7	920
San Juan	W	31.3	0.9	68
	B	60.4	1.8	136
Los Robles	W	304	5.3	486
	B	444	8.2	680
Paulding	W	174	6.0	478
	B	140	4.6	371
Lone Star	W	472	8.6	814
	B	371	6.9	620
Rockwell Lime	W	--	--	446
	B	134	15.8	386

The SO_2 emission results for Rockwell Lime are an exceptional case and are not at all representative of cement kilns. At the lime plant, SO_2 emissions are deliberately not absorbed into the product because the presence of sulfur in the lime is undesirable. No significant difference in SO_2 emissions was observed between the baseline and waste fuel burns with average concentrations of 500-600 ppm during each. The test at Rockwell Lime showed that NO_x and SO_2 concentrations change simultaneously in opposite directions.[26] NO_x emissions increase with increasing O_2 input and degree of preheating while SO_2 emissions decrease under the same conditions. The same results were observed in the Paulding test during the waste fuel burn. NO_x and SO_2 concentrations tracked together with swings in the opposite direction. At times the swings were several hundred of ppms in amplitude for both NO_x and SO_2 over 1- to 2-hour periods.[19]

These test results suggest several conclusions about the effects of waste combustion on NO_x and SO_2 emissions.

- The substitution of low sulfur waste for the sulfur-containing waste fuel can decrease SO_2 emissions when the waste fuel is burned.

- SO_2 emissions are very dependent upon the specific operating conditions of the kiln. Consequently, variations in SO_2 concentrations are observed at the same kiln over time as operating conditions change, and the variability increases from kiln to kiln because of differences in primary fuel, kiln design, and operating conditions.

- Factors affecting SO_2 emissions apparently include:
  - Sulfur loading on the kiln
  - Alkali content of raw materials
  - O_2 input
  - Temperature
  - Competition from HCl

- NO_x emissions are not affected by waste combustion. They are affected by O_2 input, secondary to primary air ratio, and temperatures. NO_x emissions are very sensitive to minor process changes and show rapid and sometimes large responses to these changes. Consequently, NO_x concentrations have been quite variable over time at the same kiln.

- An interrelationship exists between NO_x, SO_2, and O_2 input. Continuous monitoring results indicate that shifts in NO_x concentrations are often accompanied by SO_2 swings in the opposite direction. An increase in O_2 input increases NO_x emissions and decreases SO_2 emissions.

The test data collected on calcining kilns indicate that continuous monitoring for SO_2 and NO_x at some kilns may offer several advantages. Combustion conditions may be optimized for minimum fuel consumption. Emissions may be balanced or optimized within the constraints of current regulations. Immediate responses of the continuous monitors to process changes, coupled with accumulation of some historical data, may significantly improve process control, temperature control, quality control and energy usage. The potential exists for predicting upset conditions before they occur and taking corrective actions.

A careful consideration of costs and potential benefits would be needed before any recommendation on the wholesale use of the continuous monitors could be made. However, a cost-sharing research program between a government environmental (or even energy) agency and an interested commercial company on the uses of continuous NO_x and SO_2 monitors could be to the mutual benefit of both parties.

4.9 EMISSIONS OF TOTAL HYDROCARBONS (THC) AND CARBON MONOXIDE (CO)

The results for total hydrocarbons and carbon monoxide are summarized in Table 4-18. Total hydrocarbons increased during waste fuel combustion at 3 tests, decreased at 2 tests, and remained the same at another. The consistently low THC concentrations for several different types of compounds at Stora Vika suggest that kiln operation may affect THC concentrations more than the waste type does. The levels at Rockwell Lime, which attained consistently high DRES, averaged 3.5 ppm. Similarly, the Lone Star kiln maintained consistently low levels of THC between 2.5 and 5 ppm. These data for different types of kilns and wastes fuels indicate that a well-controlled kiln can operate with average THC concentrations below 10 ppm.

CO emissions are not affected by burning waste fuels. Weitzman noted that changes in CO can be indicative of flame quenching, improper burner adjustment, or other imbalances in the flame.[11] Peters and Mournighan(26) found that any process change can create a significant CO excursion, which is often a temporary spike. Examples of process changes include changes in the primary air/fuel ratio, changes in secondary air, irregular solid fuel feed rates, and changes in the exhaust damper.[26] These effects were observed during the Paulding test during a kiln upset with coal as the only fuel.

TABLE 4-18. SUMMARY OF THC AND CO CONCENTRATIONS

Site	Test condition	THC (ppm)[a]	CO (ppm)
Marquette	Waste burn	470[b]	-
	Baseline	1,250[b]	-
San Juan	Waste burn	12.7	24 - 738[c]
	Baseline	8.3	25 - 349[c]
Los Robles	Waste burn	[d]	25 - 100
	Baseline	4	10 - 618
Paulding	Waste burn	21	190
	Baseline	10	212
Lone Star	Waste burn	5	24 - 49[c]
	Baseline	2.5	35 - 40[c]
Rockwell Lime	Waste burn	3.5	599
	Baseline	8.2	477
Stora Vika	Chlorinated aliphatics	<10	300 - 1500
	Baseline	<10	1,500
	PCBs	<10	100 - 1500
	Baseline	<10	100
	Chlorophenols/phenoxy acids	10	50 - 500
	Baseline	10	50
	Freon	<10	100 - 500
	Baseline	<10	100

[a]Expressed as ppm methane unless otherwise noted.

[b]Total nonmethane hydrocarbons.

[c]Range of test averages.

[d]Not measured.

Over the course of the event, several process parameters were changed and large swings in CO (as well as other monitored gas concentrations) were observed. The CO results for Stora Vika show a range of 50-1500 ppm for both the baseline and waste fuel burns. The CO results for Lone Star appear to be the most consistently low. The kiln was operated with a higher O_2 input (to aid in drying wet coal), which apparently resulted in very consistently low levels of THC, CO and SO_2 with increased NO_x concentrations. The Los Robles kiln was also very stable during three waste firing tests in which the maximum CO was 100 ppm.

The CO results indicate that waste fuel combustion does not significantly affect CO concentrations. Process stability apparently has a greater effect on CO concentrations. CO monitors on kilns provide the operator with a measure of this stability, but only in the extreme because of high detection limits. More sensitive continuous monitoring has shown that CO spikes can be caused by minor process charges, and poor combustion conditions (e.g., kiln upset) can lead to longer and higher swings in CO.

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